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Studies on Modified Atmosphere Packaging of Fresh Produce

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Contents

General introduction

Horticultural commodities gradually deteriorate with the consumption of nutrients in the plant body in order to live even after being harvested. The control of respiration then plays an important role in prolonging the post harvest life of fresh produce. The atmosphere surrounding the fresh produce affects the rate of its respiration (Kader, 1986). Controlled atmosphere (CA) storage (Dilley, 1978) and modified atmosphere packaging (MAP) (Kader et al., 1989) systems have been adopted to control the atmospheric conditions. The respiration of fresh produce can be depressed by creating an atmosphere optimized for its storage in such systems (generally the O_2 concentration is lowered and the CO_2 concentration is elevated).

CA is the method where the atmosphere in a storehouse is maintained under a desirable condition for a commodity by continuously pumping the gas of the desired composition into the storehouse. Although an optimal atmosphere is instantly obtained, a specific apparatus is needed for this method. This means that this method is difficult to apply simultaneously to many kinds of commodities as each commodity prefers to be stored under a specific atmosphere. MAP is the method to create an optimal composition of O_2 and CO_2 by controlling the respiration of fresh produce and the gas permeation through the package film. The O_2 concentration changes in the range 0–21% in a MAP system. A high O_2 concentration near 20% causes the rapid deterioration of a packaged commodity by activating the metabolic reactions such as respiration. A horticultural commodity therefore prefers to be stored at low O_2 concentrations of under 10%. However, extremely low O_2 concentrations of under 1% create an anaerobic atmosphere which induces off-odor that reduces its quality. The initial concentration of CO_2 in a MAP system is usually 0.03%. The CO_2 concentration is often above 20% during the storage of

the commodity in a MAP system using a high-barrier film. An extremely high CO_2 concentration of over 20% will induce off-odor. The CO_2 gas is effective for prolonging the shelf life of a horticultural commodity when the concentration is controlled under the concentration that the commodity can tolerate. The CO_2 tolerability of a commodity is dependent on the kind of commodity. Some commodities prefer to be stored under 0% CO_2, for example, lettuce, tomatoes and so on. A CO_2 scrubber is enclosed in the MAP system used for CO_2 intolerable commodities. In this system, the atmosphere will be controlled under low O_2 and 0% CO_2 concentrations. Although it takes a longer time to obtain the desirable atmosphere than the CA method, this method does not need a specific apparatus as CA. This method can be applied to many kinds of commodities as the operation is simple. Packaging conditions to create an optimal atmosphere, for example, type, surface area and thickness of the packaging film and weight of the commodity, need to be rapidly selected using a microcomputer. For that purpose, rates of respiration of the commodity and transmission of gases through the package need to be modelled as mathematical forms. Models for the gas transmission rate through a film have already been proposed on the basis of Fick's first law of diffusion and Henry's law of gas solubility.

Respiration models have been studied since the 1970s. Henig and Gilbert (1975) used a specific model for the respiration of tomatoes to predict the atmosphere in a package where the respiration rate was linearly dependent on O_2 concentration in the range 4–11.53% and constant in the O_2 range 11.53–21%. Hayakawa et al. (1975) modified the model (Henig and Gilbert, 1975) by expressing the respiration rate of tomatoes and bananas as a function of both the O_2 and CO_2 concentrations. Yang and Chinnan (1988) and Sato et al. (1993) expressed the respiration of tomatoes and broccoli as a function of the O_2 and CO_2 concentrations, and the storage time using non-linear regression analysis. Cameron et al. (1989) described the O_2 consumption rate of tomatoes as a function of the O_2 concentration surrounding tomatoes using an exponential-type equation. These

respiration models mentioned above will be effective under limited storage conditions as they are modelled by empirical approaches. Lee et al. (1991) proposed that the Michaelis-Menten-type equation (Michaelis and Menten, 1913) was suitable for modelling the aerobic respiration of six types of fresh produce. The respiration process composed of many metabolic reactions is described by an enzyme kinetic model.

Some models for the temperature dependence of the respiration of fresh produce have been proposed as the respiration rate changes with storage temperature (Ryall and Lipton, 1979; Ryall and Pentzer, 1982). Beaudry et al. (1992) expressed the temperature dependence of the O_2 consumption of blueberries using an exponential-type equation. Talasila et al. (1992) described the O_2 consumption rate of strawberries as a product of a non-linear regression model including five variables and an exponential-type equation expressing the temperature dependence of the O_2 consumption rate. Morales-Castro et al. (1994a, b) expressed the temperature dependence of the O_2 consumption of sweet corn and head lettuce using non-linear regression models. These models will be effective under limited conditions as they are modelled by empirical approaches. It has been indicated that the Arrhenius equation is suitable for expressing the temperature dependence of respiration of fresh produce. Karel and Go (1964), Haggar et al. (1992) and Song et al. (1992) proposed that the Arrhenius equation can be applied to the respiration of bananas, broccoli and blueberries, respectively. Joles et al. (1994) attempted to describe theoretically the O_2 consumption of raspberries as a product of the Michaelis-Menten equation proposed by Lee et al. (1991) and a temperature coefficient (Q_{10}). However, this model is not effective under an atmosphere with CO_2, and the effectiveness of the model for predicting the atmosphere in MAP was not also confirmed.

The prediction of dynamic changes in the atmosphere during MAP of fresh produce has been attempted since the 1960s. Jurin and Karel (1963) determined the O_2 and CO_2 concentrations surrounding apples in a MAP system with low density polyethylene (LDPE)

film under a steady-state condition using a graphical method. The respiratory quotient (*RQ*) of apples is then assumed as unity. Verraju and Karel (1966) determined the optimal packaging condition for apples by the graphical method using some types of packaging materials. Henig and Gilbert (1975) and Hayakawa et al. (1975) calculated the gas concentrations in MAP systems including tomatoes and bananas with polymeric films under steady- and unsteady-state conditions by computer simulation, respectively. Deily and Rizvi (1981) determined a gas composition in a MAP system of peaches using a specific respiration model where the rate of respiration was constant in the O_2 range 5–21% and the CO_2 range 0–25%. Lee et al. (1991) simulated the O_2 and CO_2 concentrations in MAP of broccoli with a LDPE pouch under an unsteady-state condition. Sato et al. (1993) predicted the atmosphere in MAP of broccoli under steady- and unsteady-state conditions.

The range of atmosphere obtained by MAP with polymeric films is limited. A CO_2-enriched atmosphere in a MAP system is difficult to be created as the transmission rate of CO_2 through a permeable film is usually higher than that of O_2. An anaerobic condition including an excessive concentration of CO_2, which caused the production of off-odor, is induced in a MAP system with a high-barrier film. Micro-perforated films have been developed to avoid inducing an anaerobic atmosphere. The micro-perforated film is indicated to be applicable to MAP for many kinds of commodities (Mannapperuma and Singh, 1993). Emond et al. (1991) modelled the transmission of a gas through a perforation as a function of the thickness and diameter of a perforation, and the temperature using non-linear regression analysis. They reported that the composition of 9% O_2 and 12.5% CO_2, which is desirable for the storage of strawberries, is obtained using the model. Renault et al. (1994a) attempted to express the gas transmission through a perforation using the Stephan-Maxwell equation and predict the atmosphere in MAP of strawberries with a micro-perforated package.

In the present study, attempts to propose effective models to predict the atmosphere in MAP systems are made. This study can be separated into two parts. In the first part, attempts to describe effectively the O_2 consumption of fresh produce are made. The suitability of the proposed O_2 consumption models for the actual O_2 consumption rate data for horticultural commodities is examined in this part. Derivation of an O_2 consumption model on the basis of the adsorption theory of Langmuir (1918) is described in Chapter 1. The model proposed in Chapter 1 is modified to a model effective under an atmosphere with CO_2 based on a biochemical mechanism in Chapter 2. Derivation of a model expressing the temperature dependence of O_2 consumption on the basis of the transition state theory is proposed in Chapter 3.

The prediction of the atmosphere in MAP systems of some packaging materials using the O_2 consumption models proposed in the first part is attempted in the second part. A simple method for the determination of gas permeability of a packaging material, which is needed for the prediction of atmosphere in MAP systems, is developed in Chapter 4. The atmosphere in MAP systems with polymeric pouches is predicted in Chapter 5 using the O_2 consumption models proposed in the first part. The expression of gas transmission through a perforation is described in Chapter 6 based on the kinetic molecular theory of gases. The atmosphere in MAP systems with a micro-perforated film is predicted in the same chapter. The permeation of gases through a biodegradable film is examined in Chapter 7. The prediction of the atmosphere in MAP systems with the biodegradable film is carried out in the same chapter.

PART I

Models for respiration of fresh produce

Chapter 1

Oxygen consumption model for fresh produce on the basis of adsorption theory

1.1 Introduction

The crucial important knowledge for designing MAP is the exact model expression for the respiration of fresh produce. As described in the general introduction, many researchers have proposed the expressions of the respiration of fresh produce so far. However, the expressions were not adequate in view of theoretical and experimental points. In this chapter, a theoretical model was proposed for representing O_2 consumption caused by the respiration of fresh produce. The O_2 consumption rate equation was derived from the adsorption theory proposed by Langmuir (1918), and its suitability for predicting respiration rates for various kinds of fresh produce was evaluated.

1.2 Theoretical considerations

The number of O_2 molecules adsorbed on active sites in fresh produce per hour can be given by multiplying the O_2 concentration in a unit cell of the produce by the number of bare sites. The adsorption rate of O_2 molecules is expressed as follows:

$$V_a = K_a C_O (1-\theta) N_T \qquad (1\cdot1)$$

where V_a is the adsorption rate of O_2 molecules (molecules·kg^{-1}·h^{-1}), C_O is the O_2 concentration in a unit cell (mmol·kg^{-1}), θ is the fraction of active sites occupied by O_2 molecules (—), K_a is the mean value of the proportionality constant (kg·mmol^{-1}·h^{-1}), and N_T is the total number of active sites (molecules·kg^{-1}).

The mean value of the proportionality constant (K_a) which represents the affinity is expressed as follows, because each active site is considered to have its own affinity:

$$\frac{\sum_{J=1}^{n} k_{aJ} x_J}{\sum_{J=1}^{n} x_J} = K_a \tag{1·2}$$

where k_{aJ} is the proportionality constant of Jth type of the active site (kg·mmol^{-1}·h^{-1}), x_J is the number of Jth type of the active site (molecules), and n is the number of types of active sites.

The O_2 concentration in a unit cell is assumed to be proportional to the O_2 partial pressure, according to Henry's law, which describes the solubility of gas into liquid. The O_2 concentration [C_O (mmol·kg^{-1})] is given as follows:

$$C_O = S_O p_O \tag{1·3}$$

where S_O is the proportionality constant (mmol·kg^{-1}·kPa^{-1}), and p_O is the partial pressure of O_2 gas surrounding the fresh produce (kPa).

According to the adsorption theory by Langmuir (1918), the number of gas molecules desorbed from active sites per hour is proportional to the number of adsorbed gas molecules. The desorption rate of O_2 molecules which were adsorbed on active sites in fresh produce can be expressed as follows:

$$V_d = K_d \theta N_T \tag{1·4}$$

where V_d is the desorption rate of the adsorbed O_2 molecules (molecules·kg^{-1}·h^{-1}), and K_d is the mean value of the proportionality constant (h^{-1}).

The mean value of the proportionality constant (K_d) which describes the rate of desorption can be given as follows:

$$\frac{\sum_{J=1}^{n} k_{dJ} x_J}{\sum_{J=1}^{n} x_J} = K_d \tag{1·5}$$

where k_{dJ} is the proportionality constant of Jth type of the active site (h^{-1}).

At equilibrium, the rate of adsorption equals that of desorption, hence $V_a = V_d$. From Eqs. 1·1, 1·3 and 1·4, the fraction of the active sites occupied by O_2 molecules (θ) can be calculated as follows:

$$\theta = \frac{a p_O}{1 + a p_O} \tag{1·6}$$

where $S_O K_a K_d^{-1}$ is replaced by the parameter a (kPa^{-1}).

θ is also expressed as $\theta = N_A / N_T$ because θ is defined as the fraction of active sites occupied by O_2 [N_A is the number of O_2 molecules adsorbed on the active sites (molecules·kg^{-1})].

From Eq. 1·4, the O_2 desorption (or consumption) rate (V_d) is also equal to $K_d N_A$. The O_2 consumption rate [R_O (mmol·kg^{-1}·h^{-1})], therefore, can be represented as follows:

$$R_O = \frac{K_d N_A}{L} \tag{1·7}$$

where L is the Avogadro's constant 6.022×10^{20} molecules·mmol^{-1}.

In the same manner as above, the maximum O_2 desorption (or consumption) rate must be given as $K_d N_T$ (θ = 1 in Eq. 1·4). The maximum O_2 consumption rate [b (mmol·kg^{-1}·h^{-1})], therefore, can be given as follows:

$$b = \frac{K_d N_T}{L} \tag{1·8}$$

From Eqs. 1·6–1·8, R_O can be derived as follows.

$$R_O = \frac{abp_O}{1 + ap_O} \tag{1·9}$$

From these equations mentioned above, the O_2 consumption rate equation for fresh produce is obtained.

Equation 1·9 can be modified to a linear form given as follows.

$$\frac{p_O}{R_O} = \frac{1}{ab} + \frac{1}{b} p_O \tag{1·10}$$

The values of a and b are obtained from the slope ($1/b$) and the intercept ($1/ab$) of p_O/R_O versus p_O plots.

1.3 Materials and methods

1.3.1 Fresh produce

Lettuce (variety 'Cisco') purchased from a wholesale market in Takamatsu (Kagawa Prefecture, Japan) was shredded into square pieces (9cm^2). The shredded lettuce was washed twice in a stainless-steel pan and rinsed for 1 min with a water shower. The water adhered to the surface of the lettuce was removed by centrifugation (64.1 m·s^{-2}, 30 s). The prepared lettuce was stored at 15°C for 30 min in an incubator prior to the measurement of the O_2 consumption rate.

Tomatoes (variety 'Momotaro', the mean weight 0.107 kg) and broccoli (variety 'Naomidori', the mean weight 0.263 kg) purchased also from a wholesale market in Takamatsu were stored at room temperature for one day prior to the measurement of the O_2 consumption rate.

1.3.2 Test gas mixtures

The test gas mixtures, which contained the O_2 concentrations of 2, 5, 10, 15, and 21%, were prepared for the measurement of the O_2 consumption rate. Each of them was adjusted to 100% with N_2 gas, and pressurized in a gas cylinder (Taiyo Sanso Inc., Ebina, Japan).

1.3.3 Measurement of O_2 consumption rate

Flexible packages made of laminated film (Tamapoly Inc., Tokyo, Japan; LDPE/aluminum/LDPE/polyester) were used for the measurement of the O_2 consumption rate for shredded lettuce. The package with 0.1 kg of the shredded lettuce was closed by heat-sealing just after flushing with the test gas mixture. The void volume of the package was determined by subtracting the volume of the shredded lettuce from that of the entire package. The volume of the shredded lettuce was calculated by postulating its density as 1 g·cm^{-3}. The entire package volume was determined by the water displacement method. To

determine the initial O_2 concentration in a package, 0.4-mL gas was sampled with a gas tight syringe through the septum on the package, and analyzed by gas chromatography (GC) according to the method of Yamashita et al. (1989). Oxygen concentration in the package was determined again after incubating for 30 min at 15°C.

The O_2 consumption rate of the shredded lettuce was calculated from the consumed O_2 concentration within the package, the void volume, and the incubation time of 30 min. The calculated O_2 consumption rate was converted from a volumetric rate ($mL \cdot kg^{-1} \cdot h^{-1}$) to a molar rate ($mmol \cdot kg^{-1} \cdot h^{-1}$) by using the van der Waals equation.

In the measurement of the O_2 consumption rate, the amount of O_2 and N_2 gas permeating through the laminated film for 30 min was assumed to be negligible, because of the very small values of O_2 and N_2 gas permeability coefficients of the film employed. The permeability values were less than 1.25×10^{-9} $mmol \cdot m^{-1} \cdot h^{-1} \cdot kPa^{-1}$ at 15°C.

Figure 1·1 shows the experimental apparatus for the measurement of the O_2 consumption rate for tomatoes. Sixty-eight pieces of tomato (total weight 7.3 kg) were kept in a desiccator (volume 24,400 mL), which was covered with aluminum foil to cut off exposure to white light, and the following operations were done to replace the air in the desiccator (no.7) with one of the test gas mixtures (no.1). The gas mixture first passed through water (no.5, weak acidity) to be humidified. The humidified gas mixture was flushed from the inlet valve (no.6) to the outlet valve (no.10) for 15 min. After the flushing operation, the inlet and outlet valves were shut. The gas pressure inside the desiccator was adjusted to the atmospheric pressure by opening the outlet valve for ca. 10 s. 0.4-mL gas mixture was taken from the sampling port (no.9), and the O_2 concentration was determined. After incubating for 90 min at room temperature (16°C), the gas was sampled again and the O_2 concentration was measured. The average value of O_2 partial pressure between 0 and 90 min was used for the calculation of parameters as an independent variable in Eq. 1·10. From the void volume of the desiccator and the

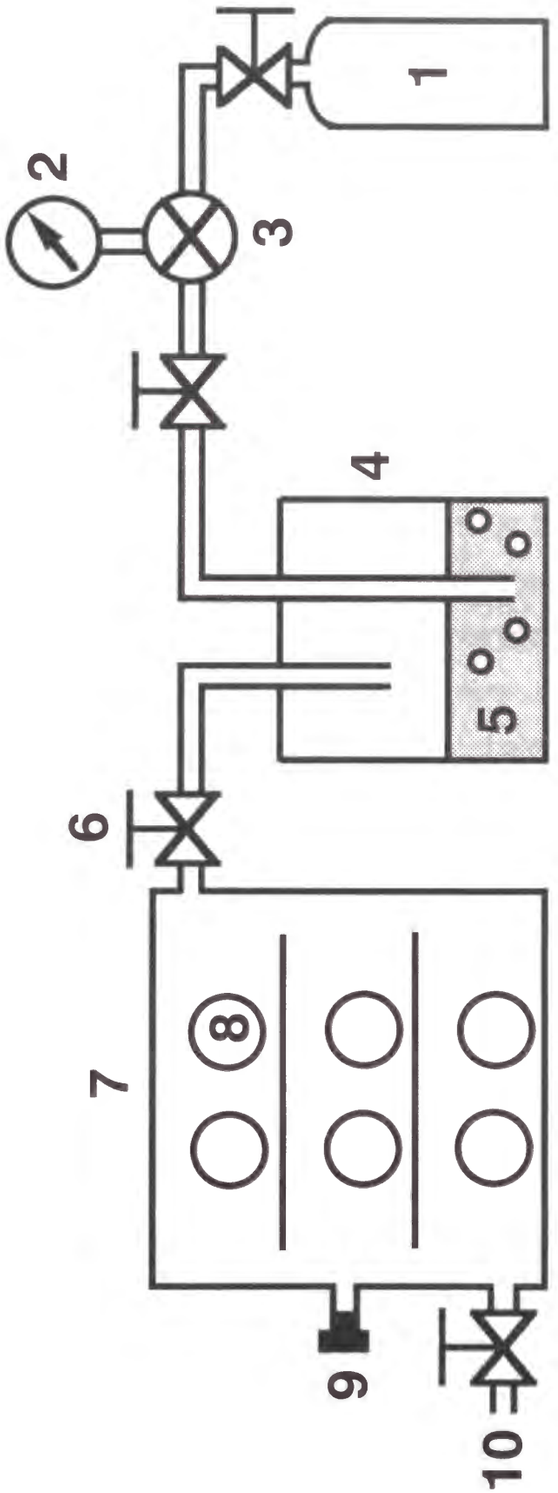

Fig. 1·1 Schematic diagram of the experimental apparatus for the O_2 consumption rate measurement of the fresh produce. 1 mixed gas cylinder, 2 pressure gauge, 3 pressure control valve, 4 water tank, 5 water of weak acidity, 6 inlet valve, 7 desiccator, 8 fresh produce, 9 gas sampling port, 10 outlet valve.

consumed O_2 concentration for 90 min, the O_2 consumption rate of the tomatoes was calculated by the same method as that used for the shredded lettuce.

The O_2 consumption rate for broccoli was measured using ten pieces of broccoli (total weight 2.63 kg) with a similar procedure to that of the tomatoes at room temperature (16°C). The incubation time was 15 min.

The O_2 consumption rate measurements were repeated six times for each test gas mixture.

1.3.4 Calculation of parameters

Parameters a and b in Eq. 1·10 were calculated from the experimental data on the consumption rate and that of the partial pressure of O_2 gas which was given for shredded lettuce, tomatoes, and broccoli in this study. Parameters a and b were also calculated for various kinds of fresh produce from the data previously published in the literature. From the calculated results, the suitability of the proposed consumption rate equation for respiration data is discussed.

1.4 Results and discussion

1.4.1 Suitability of the O_2 consumption model for respiration of fresh produce

Figure 1·2 shows the relationship between $p_O R_O^{-1}$ and p_O of the O_2 consumption experimental data for shredded lettuce, tomatoes, and broccoli. Figure 1·3 also shows the relationship between $p_O R_O^{-1}$ and p_O in the O_2 consumption published data for apples (Fidler and North, 1967), broccoli (Lee et al., 1991), bananas (Karel and Go, 1964), and blueberries (Beaudry et al., 1992). Linear regression analysis on the present and published experimental data was completed and is shown in Figs. 1·2 and 1·3. The correlation

coefficients shown in Table 1·1 were found to be in the range 0.94–1.00, which were significant at 99.9% level of Fisher's z-transformation method with StatView® ver. 4.02 for Macintosh® (Abacus Concept, Inc., Berkeley, USA). This suggests that Eq. 1·9 or 1·10 may be applied for the prediction of the O_2 consumption rate of many kinds of fresh produce. According to this consumption model, the linear relationship was still maintained under the condition that O_2 level was close to 0% as shown in Fig. 1·3. This suggests that the O_2 consumption model may be applied to respiration for a wide range of O_2 concentrations.

In general, respiration is controlled by an elaborate interlocking system of feedback controls that coordinates the rates of glycolysis, fatty acid breakdown, the citric cycle, and electron transport (Alberts et al., 1994). The biochemical reaction of O_2 consumption in a unit cell is assumed to be that one molecule of O_2 is adsorbed on an active site of cytochrome oxidase complex buried in an inner membrane of a mitochondria, and that the O_2 molecule is desorbed from the site when it accepts four electrons, which react with the O_2 molecule, and is transformed to two molecules of H_2O (Tzagoloff, 1982). The cytochrome oxidase reaction is estimated to account for 90% of the total oxygen uptake in most cells (Alberts et al., 1994). To analyze these biochemical reactions mathematically, a very complicated model is required. From a practical point of view, a simplified expression is desirable for predicting the atmospheric condition within the package. An organism, for example fresh produce, takes up an O_2 molecule by a chemical adsorptive reaction on an active enzyme site (Tzagoloff, 1982). I therefore attempted to explain the respiration of the fresh produce on the basis of adsorption theory from a macroscopic point of view. There are generally two types of adsorption: Langmuir's equation (Langmuir, 1918) was derived from a unimolar layer of a gas adsorbed on a solid. The second type of adsorption (Brunauer et al., 1938) is that where the gas forms multimolecular layers. Cytochrome oxidase complex adsorbs one molecule of O_2 per active site (Alberts et al.,

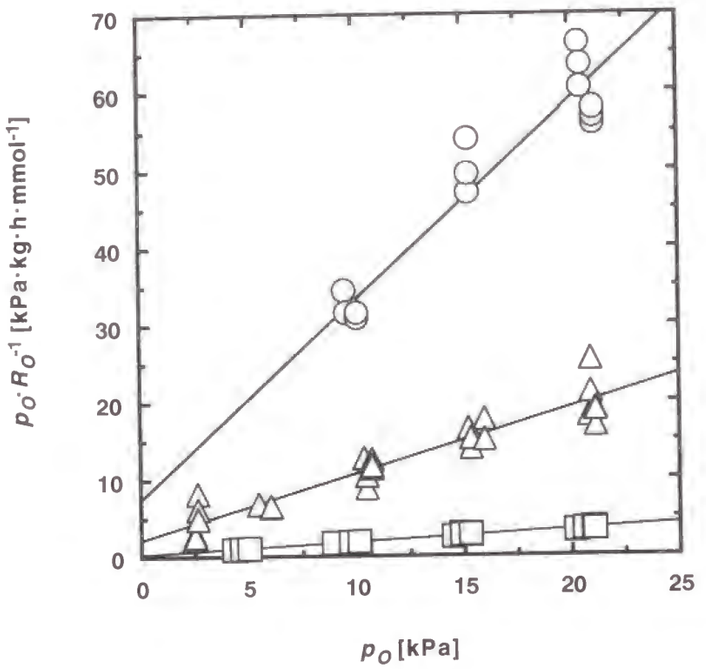

Fig. 1·2 Relationship between $p_O \cdot R_O^{-1}$ and p_O on fresh produce based on the experimental data in this study. △ Shredded lettuce, ○ tomato, □ broccoli, solid lines denote the linear regression lines.

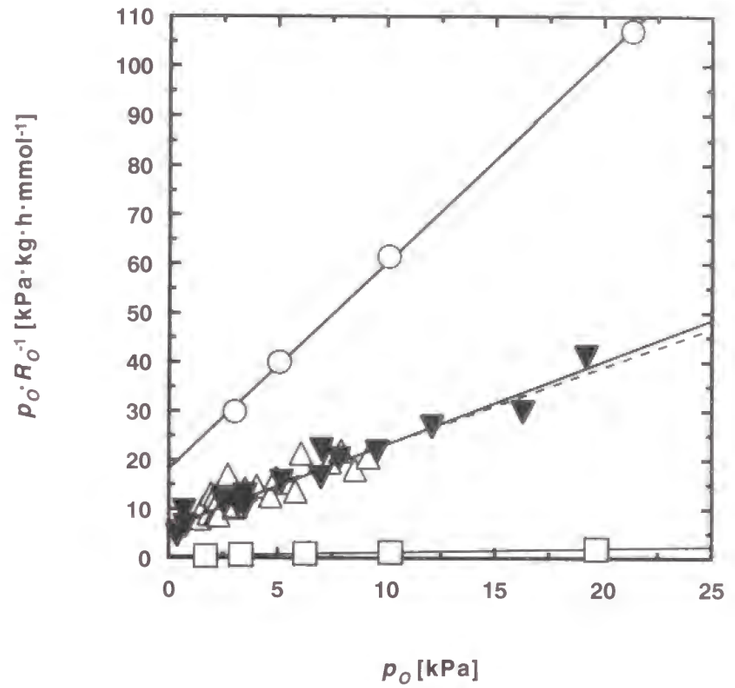

Fig. 1·3 Relationship between $p_O \cdot R_O^{-1}$ and p_O for fresh produce based on published data. ○ Apple, □ broccoli, ▼ banana, △ blueberry, solid lines denote the linear regression lines on apple, broccoli and banana. Dashed line denotes the linear regression line on blueberry.

Table 1·1 Parameters and correlation coefficients calculated from linear equations for O_2 consumption rate in fresh produce

Commodities	Temperature (°C)	Parameters		Correlation coefficients	Researchers
		a (kPa^{-1})	b (mmol·kg^{-1}·h^{-1})		
Shredded lettuce	15	0.395	1.17	0.95***	This study
Tomato	16	0.350	0.39	0.96***	This study
Broccoli	16	0.548	6.47	0.99***	This study
Apple	3.3	0.232	0.24	1.00***	Fidler and North (1967)
Broccoli	24	0.254	12.4	0.99***	Lee et al. (1991)
Banana	19	0.278	0.59	0.98***	Karel and Go (1964)
Blueberry	15	0.222	0.63	0.94***	Beaudry et al. (1992)

*** Significant at a level of 99.9% on Fisher's z-transformation

1994). I therefore attempted to derive a practical model for O_2 consumption in fresh produce based on the adsorption theory proposed by Langmuir (1918). Equations 1·7 and 1·8 imply that one molecule of O_2 is attached per active site. Equation 1·6, which is the same form as Langmuir's adsorption model (adsorption isotherm), is modified to the rate equation 1·9 for O_2 consumption with Eqs. 1·7 and 1·8. The validity of Eq. 1·9 as a rate equation was demonstrated in the present study as shown in Figs. 1·2, 1·3 and Table 1·1. Equation 1·9 is a simplified mathematical form of the enzyme kinetic model proposed by Lee et al. (1991). The validity of this mathematical form has already been demonstrated by Lee et al. (1991). In this study, I observed that the same mathematical equation form can be derived using either the enzyme kinetic theory or the adsorption theory, as the controlling mechanism.

1.4.2 Evaluation of rate parameters

Values of parameters a and b obtained from the experimental and published data are shown in Table 1·1. The a values were found to be in the range 0.222–0.548 kPa^{-1}. As described in the section 1.2, the parameter a is equal to $S_O K_a K_d^{-1}$. The a value increases with an increase in the proportionality constant S_O. The solubility of O_2 in aqueous solutions is dependent on temperature, pressure and ionic strength (Atkins., 1994). S_O may vary with the commodity. This could occur if these factors differ between the two commodities. In Table 1·1, the value of a obtained from the experimental data on broccoli (0.548 kPa^{-1}) was different from that of Lee et al. (1991) (0.254 kPa^{-1}). The value of a obtained from the experimental data on tomatoes (0.350 kPa^{-1}) was different from that of broccoli (0.548 kPa^{-1}) at the same temperature of 16°C. The magnitude of the O_2 diffusion barriers of the tissue layer (Solomos, 1987) and the slice size of shredded vegetables (Shiina et al., 1988) may affect the gas exchange rate between the flesh of the commodities and the headspace. The factors mentioned above are expected to affect the values of

parameter a and the shape of p_O versus R_O curves. This suggests that the values of a are probably dependent on the type of fresh produce.

As shown in Table 1·1, the b values obtained from the experimental data on the O_2 consumption rate were found to be in the range 0.39–6.47 mmol·kg^{-1}·h^{-1} and those from the published experimental data were found to be in the range 0.24–12.4 mmol·kg^{-1}·h^{-1}. These values appear to depend on the type of fresh produce. The b values of broccoli were found to be extremely large in this study as well as in the literature. This is probably because the respiration rate of broccoli is higher than that of the other fresh commodities (Kader et al., 1989). The b value of broccoli obtained from this experiment (6.47 mmol·kg^{-1}·h^{-1}) was smaller than that reported by Lee et al. (1991) (12.4 mmol·kg^{-1}·h^{-1}). It was probably due to the difference in experimental temperature—16°C in this experiment, and 24°C in the literature. Moreover, there were differences in sample preparation—the broccoli was not cut in this experiment. Indeed, Kader et al. (1989) reported that temperature and/or cutting treatment affects the respiration rate of fresh produce. The physiological stage of the commodity is also very important. Preclimacteric hard green bananas were used for the determination of O_2 uptake rate in the literature (Karel and Go, 1964). The value of b for bananas is expected to be higher, unless the fruits are at the preclimacteric stage (Ryall and Lipton, 1979).

1.5 Conclusions

An O_2 consumption model based on Langmuir adsorption theory was constructed in order to design the MAP systems for the storage of fresh produce. The O_2 consumption rate data for shredded lettuce, tomatoes and broccoli obtained from this study and on apples, broccoli, bananas and blueberries obtained from the literature were analyzed by the linear-type equation derived from the proposed model by the linear regression method. All

the correlation coefficients obtained were significant at a 99.9% level of Fisher's z-transformation method. The model was found to be suitable for describing the O_2 consumption of several kinds of fresh produce.

Chapter 2

A theoretical model for oxygen consumption in fresh produce under an atmosphere with carbon dioxide

2.1 Introduction

A practical model based on Langmuir's adsorption theory for the O_2 consumption in fresh produce was proposed (Makino et al., 1996a) in Chapter 1. The model was found to be suitable for describing O_2 consumption in many kinds of fresh produce, and valid for the design of the MAP system. However, the model was derived for an atmosphere containing a negligible amount of CO_2. Kader (1986) reported that CO_2 gas depresses the respiration of fresh produce. The model used, therefore, needed to be modified for explaining the O_2 consumption in fresh produce, in gaseous environments containing CO_2.

The O_2 consumption model with respiratory depression effect by the CO_2 gas is proposed for representing the respiration of fresh produce from a theoretical point of view. The previously proposed O_2 consumption model (Makino et al., 1996a) was modified on the basis that the oxidation of the organic acids in the tricarboxylic acid (TCA) cycle is inhibited by CO_2 molecules. The O_2 consumption was measured for various fresh produce subjected to an atmosphere with/without CO_2 gas, and the suitability of the modified model was evaluated.

2.2 Theoretical considerations

2.2.1 O_2 consumption rate with the depression effect of CO_2 gas

The number of O_2 molecules adsorbed on active sites in fresh produce per hour is calculated by multiplying the O_2 concentration in a unit cell of the produce by the number of bare sites. The adsorption rate of the O_2 molecules (V_a) is expressed by Eq. 1·1. The O_2 concentration in a unit cell is assumed to be proportional to the O_2 partial pressure, according to Henry's law, which describes the solubility of gas in liquid. The O_2 concentration (C_O) is given by Eq. 1·3.

Miller and Hsu (1965) reported that CO_2 does not directly inhibit the reaction of cytochrome c oxidase including the active sites. They also reported that CO_2 caused decreased oxidation and phosphorylation rates with TCA cycle acid substrates and with NADH which promote the desorption of O_2 molecules from the active sites. The CO_2, therefore, indirectly causes the desorptive inhibition of the O_2 molecules already adsorbed on the active sites. When some of the O_2 molecules adsorbed on the active sites are assumed to be inhibited from desorbing from these sites, the fraction θ can be divided into two types of the fractions: θ_f the fraction of the adsorbed O_2 molecules which can freely desorb from the active sites and θ_i the fraction of the adsorbed O_2 molecules which are inhibited from desorbing from these sites.

$$\theta = \theta_f + \theta_i \tag{2·1}$$

According to the adsorption theory by Langmuir (1918), the number of gas molecules desorbed from the active sites per hour is proportional to the number of the adsorbed gas molecules which can freely desorb from the active sites. The desorption rate of the O_2 molecules which were adsorbed on the active sites in fresh produce (V_d) can be expressed as follows:

$$V_d = K_d \theta_f N_T \tag{2·2}$$

When the number of the O_2 molecules indirectly inhibited from desorbing from the active sites per hour [V_i (molecules·kg^{-1}·h^{-1})] is assumed to be proportional to the CO_2 concentration in a unit cell and the number of the adsorbed O_2 molecules which can freely desorb, V_i can be expressed as follows:

$$V_i = K_i C_C \theta_f N_T \tag{2·3}$$

where K_i is the proportionality constant which expresses the magnitude of the desorptive inhibition (kg·mmol^{-1}·h^{-1}), and C_C the CO_2 concentration in a unit cell (mmol·kg^{-1}).

In the same manner as Eq. 1·3, the following equation is given when the CO_2 concentration (C_C) in a unit cell is assumed to be proportional to the CO_2 partial pressure according to Henry's law.

$$C_C = S_C p_C \tag{2·4}$$

where S_C is the proportionality constant (mmol·kg^{-1}·kPa^{-1}) and p_C the partial pressure of the CO_2 gas surrounding the fresh produce (kPa).

When the number of the adsorbed O_2 molecules discharged from the desorptive inhibition per hour [V_f (molecules·kg^{-1}·h^{-1})] is assumed to be proportional to the number of the O_2 molecules which is already inhibited, the following equation is obtained.

$$V_f = K_f \theta_i N_T \tag{2·5}$$

where K_f is the proportional constant which expresses the rate of the discharge from the desorptive inhibition (h^{-1}).

At equilibrium the rate of adsorption is equal to that of desorption and the rate of inhibition equal to that of discharge, hence $V_a = V_d$ and $V_i = V_f$.

θ_f can be calculated from Eqs. 1·1, 1·3 and 2·1–2·5.

$$\theta_f = \frac{ap_O}{1 + ap_O + aip_O p_C} \tag{2·6}$$

where $S_O K_a K_d^{-1}$ and $S_C K_i K_f^{-1}$ are replaced by parameters a (kPa^{-1}) and i (kPa^{-1}), respectively.

θ_f is also expressed as $\theta_f = N_A / N_T$ because θ_f is defined as the fraction of the active sites occupied by O_2 molecules which can freely desorb from the sites [N_A is the number of the adsorbed O_2 molecules which can freely desorb (molecules·kg^{-1})].

An active site releases a product instead of an O_2 molecule as a desorptive reaction, which is equivalent to O_2 consumption. From Eq. 2·2, the O_2 desorption (or consumption) rate (V_d) is also equal to $K_d N_A$. The O_2 consumption rate (R_O) therefore can be represented by Eq. 1·7.

In the same manner as above, the maximum O_2 desorption (or consumption) rate is given as $K_d N_T$ ($\theta_f = 1$ in Eq. 2·2). The maximum O_2 consumption rate (b) therefore can be given by Eq. 1·8.

From Eqs. 1·7, 1·8 and 2·6, R_O can be derived as follows:

$$R_O = \frac{abp_O}{1 + ap_O + aip_O p_C} \tag{2·7}$$

The equation for the O_2 consumption rate of fresh produce including respiratory depression by the CO_2 gas is obtained from the above equations.

2.2.2 O_2 consumption rate parameter

Equation 2·7 can be modified to a linear form as given below:

$$\frac{1}{R_O} = \frac{1}{b} + \frac{1}{abp_O} + \frac{i}{b}p_C \tag{2·8}$$

The following equations for calculation of the parameters a, b and i can be obtained and the derivation is given in the Appendix.

$$a = \frac{A_{p1}p_1 - A_{p2}p_2}{p_1p_2\left(A_{p2} - A_{p1}\right)} \tag{2·9}$$

$$b = \frac{p_1 - p_2}{A_{p1}p_1 - A_{p2}p_2} \tag{2·10}$$

$$i = \frac{B\left(p_1 - p_2\right)}{A_{p1}p_1 - A_{p2}p_2} \tag{2·11}$$

where p_1, p_2 are the constant O_2 partial pressure levels surrounding fresh produce (kPa), A_{p1}, A_{p2} (kg·h·mmol^{-1}) and B (kg·h·mmol^{-1}·kPa^{-1}) the constants.

2.3 Materials and methods

2.3.1 Fresh produce

Cabbage (variety YR-Aoba) purchased from a wholesale market in Takamatsu (Kagawa Prefecture, Japan), was shredded to 1 mm width with a cooking cutter (CQ-34R, Toshiba Inc., Tokyo, Japan). The shredded cabbage was washed twice in a stainless-steel

pan and rinsed for 1 min with a water shower. The water adhering to the surface of the cabbage was removed by centrifugation (64.1 m·s^{-2} for 30 s). The prepared cabbage was stored at 15°C for 30 min in an incubator prior to the measurement of O_2 consumption and CO_2 evolution rates.

Tomatoes (variety Momotaro) and broccoli (variety Naomidori) purchased also from a wholesale market in Takamatsu were stored at room temperature for one day prior to the measurement of O_2 consumption rate.

2.3.2 Test gas mixtures

Twelve kinds of test gas mixtures, which included combinations of three levels of O_2 concentrations (2, 10, and 21%) and four levels of CO_2 concentrations (0, 3, 6, and 9%), were prepared for the measurement of O_2 consumption rate. Each of them was adjusted to 100% with N_2 gas, and pressurized in a gas cylinder (Taiyo Sanso Inc., Ebina, Japan).

2.3.3 Measurement of O_2 consumption and CO_2 evolution rates

Flexible packages made of tetra-layer (LDPE/aluminum/LDPE/polyester) laminate (Tamapoly Inc., Tokyo, Japan) were used for the measurement of O_2 consumption and CO_2 evolution rates for shredded cabbage. The package with 0.1 kg of the shredded cabbage was heat-sealed just after flushing with the test gas mixture. The void volume of the package was determined by subtracting the volume of the shredded cabbage from that of the entire package. The volume of the shredded cabbage was calculated by postulating its density as 1 g·cm^{-3}. The entire package volume was determined by the water displacement method. To determine the initial O_2 and CO_2 concentrations in a package, 0.4 mL was sampled with a gas tight syringe through a silicone rubber septum (1 cm × 1 cm square) glued on the package, and analyzed according to the method of Yamashita et al.

(1989) using a gas chromatograph equipped with a thermal conductivity detector (Yanaco G-2800, Yanagimoto Inc., Kyoto, Japan). Oxygen and CO_2 concentrations in the package were determined again after incubating for 15 min at 15°C.

The O_2 consumption and CO_2 evolution rates of the shredded cabbage were calculated from the concentrations of O_2 consumed and CO_2 evolved within the package, the void volume, and the incubation time of 15 min. The calculated O_2 consumption and CO_2 evolution rates were converted from volumetric rates ($mL \cdot kg^{-1} \cdot h^{-1}$) to molar rates ($mmol \cdot kg^{-1} \cdot h^{-1}$) by using van der Waals equation (Atkins, 1994).

In the measurement of O_2 consumption and CO_2 evolution rates, the amounts of the O_2, CO_2 and N_2 gases permeating through the laminated film for 15 min were assumed to be negligible due to the very small values of O_2, CO_2 and N_2 gas permeability coefficients of the film employed which were less than 5.0×10^{-9} $mmol \cdot m^{-1} \cdot h^{-1} \cdot kPa^{-1}$ at 15°C.

The O_2 consumption rates of the tomatoes and broccoli were determined by the method of Makino et al. (1996a). In the measurement of the O_2 consumption rates, Sixty-eight pieces of tomato (total mass 7.3 kg) and ten pieces of broccoli (total mass 2.63 kg) were used. The O_2 consumption rates were measured at room temperature (16 °C).

The O_2 consumption and CO_2 evolution rate measurements were repeated six times for each test gas mixture.

2.3.4 Determination of rate parameters

Parameters a, b and i for the shredded cabbage were calculated by Eqs. 2·9–2·11. The values of the parameters a and b for the tomatoes (this study), the broccoli (this study) and the broccoli (Lee et al., 1991), which had been presented in the previous paper (Makino et al., 1996a), were also used for the respiration data analysis in this chapter and substituted in Eq. 2·11 for the calculation of parameter i. Linear regression analysis, where the independent variable was the CO_2 partial pressure in headspace and the

dependent variable was the reciprocal of the O_2 consumption rate, was conducted on each product and at each O_2 partial pressure. The significance of the correlation coefficients obtained from the analysis was estimated by Fisher's z-transformation method with StatView® ver. 4.02 for Macintosh® (Abacus Concepts, Inc., Berkeley, USA).

2.4 Results and discussion

2.4.1 Suitability of O_2 consumption model for respiration

Figure 2·1 shows the relationship between R_O^{-1} and p_C in the O_2 consumption experimental data for shredded cabbage, tomatoes, and broccoli in this study, and those in the published O_2 consumption experimental data for broccoli (Lee et al., 1991). The value of $1/R_O$ for the broccoli obtained from this study was larger than that obtained from the literature (Lee et al., 1991). This is probably due to the difference of experimental temperature: 16°C in this experiment, and 24°C in the literature, and to that of the sample preparation which was whole in this experiment and cut in the literature. Kader et al. (1989) reported that temperature and/or cutting treatment affects the respiration rate of fresh produce. The correlation coefficients between the experimental data and the straight fit lines are shown in Table 2·1 and were found to be in the range 0.587–0.902, and those were significant at 95% level of the Fisher's z-transformation except for one coefficient. This suggests that Eq. 2·7 or 2·8 may be applied for the prediction of O_2 consumption rates of three kinds of fresh produce. The O_2 consumption data from the literature (Lee et al., 1991) for broccoli at 12.7 kPa of O_2 partial pressure resulted in correlation coefficient which was not significant at the 95% level. However, the experimental data substituted in Eq. 2·8 are obviously linear as shown in Fig. 2·1.

In general, respiration is controlled by an elaborate interlocking system of feedback controls that coordinate the rates of glycolysis, fatty acid breakdown, the citric cycle and

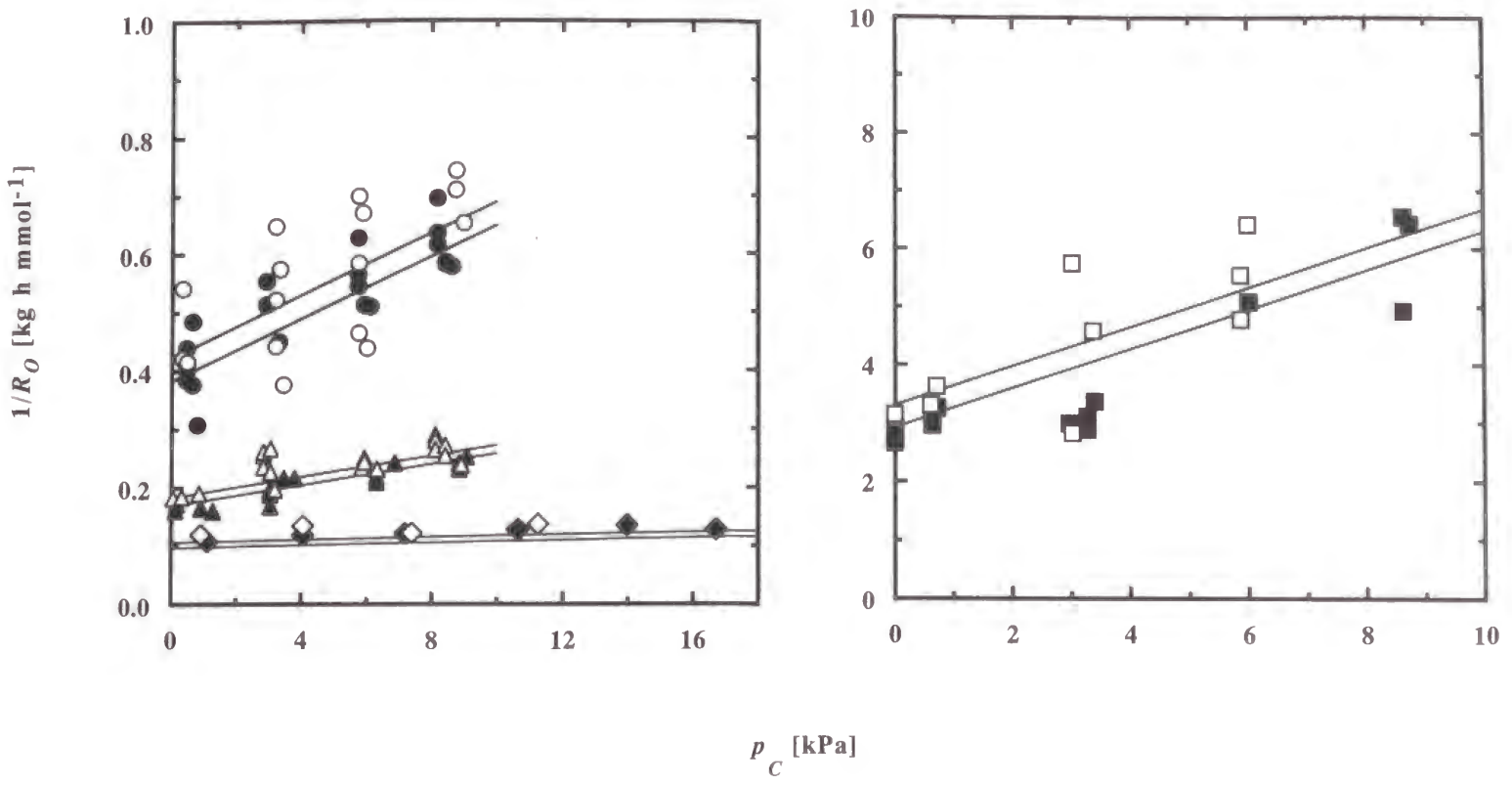

Fig. 2·1 Relationship between the reciprocal of the O_2 consumption rate (R_O) and the partial pressure of CO_2 (p_C) for fresh produce based on the experimental data from this study and the literature (Lee et al., 1991). From this study: ○ Shredded cabbage at 2.03 kPa O_2, ● Shredded cabbage at 21.3 kPa O_2, △ Broccoli at 10.1 kPa O_2, ▲ Broccoli at 21.3 kPa O_2, □ Tomato at 10.1 kPa O_2, and ■ Tomato at 21.3 kPa O_2. From the literature (Lee et al., 1991): ◇ Broccoli at 12.7 kPa O_2 and ◆ Broccoli at 21.3 kPa O_2. Solid lines denote straight fit lines.

Table 2·1 Correlation coefficients, slopes, and intercepts calculated from linear regression of O_2 consumption rate in fresh produce

Commodities	Temperature (°C)	O_2 pressure (kPa)	Correlation coefficients	Slope	Intercept
Shredded cabbage	15	2.03	0.653***	2.65×10^{-2}	0.422
Shredded cabbage	15	21.3	0.848***	2.65×10^{-2}	0.382
Tomato	16	10.1	0.823***	3.39×10^{-1}	3.290
Tomato	16	21.3	0.902***	3.39×10^{-1}	2.910
Broccoli	16	10.1	0.773***	8.79×10^{-3}	0.182
Broccoli	16	21.3	0.897***	8.79×10^{-3}	0.168
Broccoli†	24	12.7	0.587^{NS}	1.08×10^{-3}	0.106
Broccoli†	24	21.3	0.894*	1.08×10^{-3}	0.096

*** Significant at a level of 99.9%, * ; 95%, and ^{NS}; not significant using Fisher's z-transformation method

† Published data (Lee et al., 1991)

electron transport (Alberts et al., 1994). The biochemical mechanism for O_2 molecule consumption in a unit cell is recognized to be that one molecule of O_2 is adsorbed on an active site of cytochrome c oxidase buried within the membrane of a mitochondria, and that the O_2 molecule is desorbed from the site when it accepts four electrons from the electron transport chain, and is transformed (Tzagoloff, 1982) to two molecules of H_2O. The cytochrome oxidase reaction is estimated to account for 90% of the total oxygen uptake in most cells (Alberts et al., 1994). To analyze these biochemical reactions mathematically, a very complex model is needed. From a practical point of view, a simplified expression is desirable for predicting the atmospheric condition within the package during the storage and/or the transportation process of harvested fresh produce. An attempt was made to explain the O_2 consumption of the fresh produce on the basis of adsorption theory from a macroscopic point of view. There are generally two types of adsorption: Langmuir's equation (Langmuir, 1918) was derived for a unimolecular layer of a gas adsorbed on a solid. In the second type (Brunauer et al., 1938) the gas forms multimolecular layers. Cytochrome c oxidase adsorbs one molecule of O_2 at an active site, hence cytochrome a_3 in the enzyme complex (Greenwood et al., 1974). I therefore attempted to derive a practical model for O_2 consumption in fresh produce based on the adsorption theory proposed by Langmuir (1918). The most predominant opinion for respiratory depression by CO_2 is that the CO_2 molecule causes the metabolic inhibition for organic acids in the TCA cycle which is one of the most important steps in respiratory process. Hulme (1956), Bendall et al. (1958, 1960), Brown et al. (1968), Frenkel and Patterson (1973) and Knee (1973) reported that CO_2 inhibited the oxidation of succinic acid. Ranson et al. (1960), Miller and Hsu (1965), and Shipway and Bramlage (1973) found that CO_2 inhibited the oxidation of other organic acids in the TCA cycle. The inhibition reduces the formation of NADH and $FADH_2$ which are produced from NAD^+ and FAD. This indirectly reduces O_2 molecule desorption in the final step of the electron transport chain (Baldwin and Krebs, 1981).

Equation 2·6 (adsorption isotherm) is modified to the rate equation 2·7 for O_2 consumption with Eqs. 1·7 and 1·8. The validity of Eq. 2·7 as a rate equation was demonstrated in the present study as shown in Fig. 2·1 and Table 2·1. It is well accepted that CO_2 depresses the O_2 consumption of fresh produce. Equation 2·7 is a simplified mathematical form of the enzyme kinetic model with uncompetitive inhibition. The validity of this mathematical form has already been demonstrated by Lee et al. (1991) for aerobic respiration of fresh produce. In this study, it was observed that the same mathematical form equation describing the controlling mechanism can be derived incidentally using either the enzyme kinetic theory or the adsorption theory. The uncompetitive inhibition is defined as the direct inhibition of the enzymic activity where an inhibitor binds to the enzyme-substrate complex but does not bind to the free enzyme (Stenesh, 1989). Lee et al. (1991) approximated respiration rate of fresh produce with an uncompetitive inhibition model. However, many authors concluded that the mechanism for CO_2 inhibition of O_2 uptake in some manner interferes with organic acid metabolism, which is an indirect effect (Miller and Hsu, 1965). Such indirect effects resist mathematical modeling of respiration rate equations at a mechanistic level. The macroscopic approach, such as adsorption theory, which was applied to derive Eq. 2·7 may be feasible for expressing complex biochemical reactions.

2.4.2 Evaluation of O_2 consumption rate parameters

Table 2·2 shows the values of the rate parameters where the atmospheric condition is with/without the CO_2 gas. As described in section 1.2, parameter a is equal to $S_O K_a K_d^{-1}$. The value of S_O is somehow affected by components of the juice which relate to O_2 gas solubility (Atkins, 1994) and by gas diffusion pathways which limit the amount of O_2 penetrating into the skin and flesh (Solomos, 1987). However, S_O is considered to be independent of p_C. The parameters K_a and K_d may also be independent of p_C as CO_2

Table 2·2 O_2 consumption rate parameters for fresh produce

Commodity	Temperature (°C)	CO_2†	a (kPa^{-1})	b ($mmol \cdot kg^{-1} \cdot h^{-1}$)	i (kPa^{-1})
Shredded cabbage	15	+	4.20	2.57	0.0681
Shredded cabbage	15	−	4.20	2.57	—
Tomato	16	+	0.350	0.390	0.132
Tomato	16	−	0.350	0.390	—
Broccoli	16	+	0.548	6.47	0.0569
Broccoli	16	−	0.548	6.47	—
Broccoli‡	24	+	0.254	12.4	0.0134
Broccoli‡	24	−	0.254	12.4	—

† +; present, —; absent

‡ Published data (Lee et al., 1991)

does not directly inhibit O_2 consumption by cytochrome c oxidase according to Miller and Hsu (1965). The CO_2 gas therefore is not considered to affect the value of the parameter a on the same kind of fresh produce and under the same temperature as shown in Table 2·2. The a value of shredded cabbage was larger than that of the other ones as shown in Table 2·2. This is provably due to the fact that O_2 gas can easily move from the headspace into the inner cell of the cabbage due to its thin width (1 mm).

As described in section 1.2, parameter b was defined as the maximum O_2 consumption rate. The value of this parameter is affected by several factors, for example the type of commodity, ambient temperature, and physiological stage of the commodity (Ryall and Lipton, 1979). The values of b for broccoli is much larger than those of the other commodities. High O_2 uptake rate is characteristic of young tissue such as partly developed flower buds found in broccoli (Ryall and Lipton, 1979). The parameter b was also defined as a function of the total number of active sites in Eq. 1·8. Since the total number of the active sites is independent of the CO_2 concentration, the value of the parameter b does not change, hence the b value is not affected by CO_2 gas on the same kind of fresh produce and the same temperature (Table 2·2).

From the above discussion and the significance of the correlation coefficients shown in Table 2·1, the assumption that the values of the parameters a and b in Eq. 2·7 are equal to those in the previously proposed model (Makino et al., 1996a) $\{R_O=abp_O/(1+ap_O)\}$ may be valid. Equation 2·7 can be applied to the respiration in atmosphere composed of any composition of O_2, CO_2 and N_2 gases as the equation is constructed by including the term aip_Op_C in the denominator of the previously proposed equation (Makino et al., 1996a).

As described in sub-section 2.2.1, parameter i is equal to $S_CK_iK_f^{-1}$. As shown in Table 2·2, the i value obtained from the experimental data for the broccoli (0.0569 kPa^{-1}) was larger than that reported by Lee et al. (1991) (0.0134 kPa^{-1}), and i values change

depended on the type of fresh produce. S_C values which are somehow affected by the components of the juice (Atkins, 1994) and by the gas diffusion pathways in the produce (Solomos, 1987) as well as S_O values. Carbon dioxide solubility in aqueous solutions which affects the S_C value is dependent on temperature, pressure, and ionic strength (Atkins, 1994). K_i and K_f values might change with the metabolic pathways dependent on the type of the commodity (ap Rees, 1980). These imply that the magnitude of respiratory depression by CO_2 is dependent on the type of the commodity and its environment.

2.5 Conclusions

A practical O_2 consumption model for fresh produce under an atmosphere with CO_2 was derived for the design of MAP systems based on the assumption that CO_2 gas inhibits the oxidation of the organic acids in the TCA cycle. The O_2 consumption rates calculated using the proposed equation for shredded cabbage, tomatoes and broccoli agreed with the experimental data, where almost all the correlation coefficients were significant at 95% level using Fisher's z-transformation method. The respiratory depression effect for O_2 consumption in the fresh produce was discussed with the rate parameters in the proposed equation. The parameters a and b were not affected by the present of CO_2 in the headspace, while the inhibition parameter i changed with the kind of the produce.

Chapter 3

Application of transition state theory in model development for temperature dependence of respiration of fresh produce

3.1 Introduction

During postharvest handling, it is likely that a product will be exposed to varying temperature conditions. In designing a suitable packaging film for varying product temperature, consideration of respiration rate as a function of not only O_2 and CO_2, but also temperature is important. Attempts to describe the temperature dependence of O_2 consumption rate of fresh produce by transition state theory (Glasstone et al., 1941) were made. I reported in Chapter 1 and 2 that the O_2 consumption in fresh produce is explained by the adsorption theory of Langmuir (Makino et al., 1996a, b). In the present study, the O_2 consumption model derived from the adsorption theory was modified on the basis of the transition state theory (Glasstone et al., 1941). The temperature dependence of the O_2 consumption rate of four kinds of horticultural commodities is expressed theoretically and discussed from a thermodynamic point of view. No reports have been found concerning the practical respiration model of fresh produce derived from the thermodynamic theory.

3.2 Theoretical considerations

Makino et al. (1996b) proposed Eq. 2·7 as an O_2 consumption rate equation of fresh produce on the basis of the adsorption theory of Langmuir (1918). According to the van der Waals equation (Atkins, 1994), the partial pressures of O_2 and CO_2 do not change

much in the range of experimental temperatures used in this study 0–30°C. Variation in the O_2 consumption rate of the fresh produce is therefore explained as the temperature dependence of the rate parameters a, b and i in Eq. 2·7.

An O_2 molecule in a unit cell of fresh produce is adsorbed on an active site included in a cytochrome oxidase. The adsorbed O_2 molecule is consumed with four electrons producing two molecules of H_2O (Alberts et al., 1994). A CO_2 molecule reduces overall respiration rate by inhibiting the consumption of the O_2 molecule (Makino et al., 1996b; Miller and Hsu, 1965). This suggests that the consumptive reaction of the O_2 molecule is the rate determining step of the respiration activity in fresh produce. The statement also implies that modelling of temperature dependence of the O_2 consumption rate is effective for expressing respiration of fresh produce.

The consumption rate of an O_2 molecule adsorbed on an active site is expressed by Eq. 2·2. The proportionality constant K_d is a chemical kinetic constant of the O_2 consumption as the product $\theta_f N_T$ in Eq. 2·2 denotes the number of reactants (Atkins, 1994). The chemical kinetic constant is expressed by the following equation according to the transition state theory of Eyring (Glasstone et al., 1941):

$$\Delta G^{\ddagger} = -RT \ln\left(\frac{hK_d}{kT}\right) \tag{3·1}$$

where $\Delta G^{\ddagger}$ is the Gibbs energy of activation ($m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1}$); h is Planck's constant 3.98×10^{-32} $m^2 \cdot kg \cdot h^{-1}$; k is Boltzmann's constant 4.97×10^{-20} $m^2 \cdot kg \cdot K^{-1} \cdot h^{-2}$; R is the gas constant 1.08×10^{5} $m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1} \cdot K^{-1}$; and T is the absolute temperature (K).

The maximum O_2 consumption rate b in Eq. 2·7 is expressed by Eq. 1·8. The following equation is obtained from Eqs. 3·1 and 1·8:

$$\Delta G^{\ddagger} = -RT \ln\left(\frac{Lhb}{N_T kT}\right) \tag{3·2}$$

When the temperature dependence of the rate parameters a and i is assumed to be much smaller than the dependence of b, the O_2 consumption rate of fresh produce at an arbitrary temperature included in a practical range for the storage of the fresh produce is calculated using Eqs. 2·7 and 3·2.

A linear form of Eq. 3·2 is given as follows:

$$\ln\left(\frac{b}{T}\right) = -\frac{\Delta G^{\ddagger}}{RT} + \ln\left(\frac{N_T k}{Lh}\right) \tag{3·3}$$

The values of $\Delta G^{\ddagger}$ and N_T are calculated by substituting the values of parameter b obtained at several levels of temperature into Eq. 3·3 using linear regression analysis.

The Gibbs energy of activation is defined as follows (Glasstone et al., 1941):

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{3·4}$$

where $\Delta H^{\ddagger}$ is the enthalpy of activation ($m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1}$); and $\Delta S^{\ddagger}$ is the entropy of activation ($m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1} \cdot K^{-1}$).

The relationship between the enthalpy of activation and the energy of activation is as follows (Glasstone et al., 1941):

$$\Delta H^{\ddagger} = E_d - RT \tag{3·5}$$

where E_d is the energy of activation for the O_2 consumption at an active site ($m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1}$).

The relationship between a chemical kinetic constant and absolute temperature is expressed by the Arrhenius equation as follows (Atkins, 1994):

$$K_d = A_d e^{-\frac{E_d}{RT}} \tag{3·6}$$

where A_d is the frequency constant (h^{-1}).

The following equation is obtained from Eqs. 1·8 and 3·6:

$$b = \frac{A_d N_T}{L} e^{-\frac{E_d}{RT}} \tag{3·7}$$

Equation 3·7 is expressed using natural logarithms as follows:

$$\ln(b) = -\frac{E_d}{RT} + \ln\left(\frac{A_d N_T}{L}\right) \tag{3·8}$$

The values of E_d, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are calculated using Eqs. 3·3–3·5 and 3·8.

3.3 Materials and methods

3.3.1 Fresh produce

Head cabbage (variety YR-Aoba) purchased from a wholesale market in Takamatsu (Kagawa Prefecture, Japan) was shredded to 1 mm width with a cooking cutter (CQ-34R, Toshiba, Inc., Tokyo, Japan). The shredded cabbage was washed twice in a stainless-steel pan and rinsed for 1 min with a water sprinkler. The water adhering to the surface of

the cabbage was removed by centrifugation (64.1 $m \cdot s^{-2}$ for 30 s). The prepared cabbage was stored at 5, 15, 20 and 30°C for 30 min in incubators prior to the measurement of O_2 consumption and CO_2 evolution rates.

Head lettuce (variety Cisco) purchased from a wholesale market in Takamatsu was shredded to 30 mm × 30 mm square with a kitchen knife. The shredded lettuce was treated by the same method as the shredded cabbage prior to the measurement of the O_2 consumption and CO_2 evolution rates.

3.3.2 Test gas mixtures

Six kinds of test gas mixtures, which included the combinations of two O_2 concentrations [2 and 21% (partial pressures of 2.03 and 21.3 kPa under 101.325 kPa or 1 atm)] and three CO_2 concentrations [0, 3, and 9% (partial pressures of 0, 3.04 and 9.12 kPa under 101.325 kPa or 1 atm)], were prepared for the measurement of the O_2 consumption and CO_2 evolution rates. Each of them was adjusted to 100% with N_2 gas, and pressurized in a gas cylinder (Taiyo Sanso, Inc., Ebina, Japan).

3.3.3 Measurement of respiration rates

The O_2 consumption and CO_2 evolution rates of the shredded cabbage and shredded lettuce were determined by the method of Makino et al. (1996a).

A flexible pouch made of tetra-layer (LDPE/ aluminum/ LDPE/ polyester) laminate (Tamapoly, Inc., Tokyo, Japan) with 0.1 kg of the shredded cabbage or shredded lettuce was heat-sealed just after flushing with a test gas mixture. The void volume of the tetra-layer pouch was determined by subtracting the volume of the shredded cabbage or shredded lettuce from the volume of the entire tetra-layer pouch. The values of the volume of the shredded cabbage, the shredded lettuce, and the entire tetra-layer pouch were determined by the water displacement method. To determine the initial O_2 and CO_2

concentrations in the tetra-layer pouch, 0.4 mL gas was sampled with a gas tight syringe through a silicone rubber septum (10 mm × 10 mm square) glued on the tetra-layer pouch, and analyzed according to the method of Yamashita et al. (1989) using a gas chromatograph equipped with a thermal conductivity detector (Yanaco G-2800, Yanagimoto, Inc., Kyoto, Japan). The O_2 and CO_2 concentrations in the tetra-layer pouch were determined again after incubating for 15 min at 5, 15, 20 or 30°C.

The O_2 consumption and CO_2 evolution rates of the shredded cabbage or shredded lettuce were calculated from the concentrations of O_2 consumed and CO_2 evolved within the tetra-layer pouch, the void volume, and the incubation time of 15 min. The calculated O_2 consumption and CO_2 evolution rates were converted from volumetric rates ($mL \cdot kg^{-1} \cdot h^{-1}$) to molar rates ($mmol \cdot kg^{-1} \cdot h^{-1}$) using the van der Waals equation (Atkins, 1994).

3.3.4 Analysis of respiration rate data

Values of O_2 consumption rate parameters a, b and i for the shredded cabbage and shredded lettuce were calculated according to the method of Makino et al. (1996b). By substituting the values of p_O=21.3 kPa and p_O=2.03 kPa (the values of O_2 partial pressures shown in sub-section 3.3.2) into Eqs. A·2 and A·5, the relations: $A_{p1}=1/b+1/21.3ab$ and $A_{p2}=1/b+1/2.03ab$ are found. To determine the values of A_{p1}, A_{p2} and B, the method of Makino et al. (1996b) was used with values of R_O and p_C measured at 5, 15, 20 or 30°C in this study. The values of the parameters a, b and i were calculated by substituting the values of A_{p1}, A_{p2} and B into Eqs. 2·9–2·11.

Values of the O_2 consumption rate parameters a and b for blueberries (Beaudry et al., 1992) and raspberries (Joles et al., 1994) were calculated according to the method of Makino et al. (1996a). The values of the parameters a and b were calculated by linear regression analysis conducted after substituting a pair of R_O and p_O values measured at an arbitrary temperature into Eq. 1·10. The R_O and p_O values were measured at several

temperature levels in the reports previously published (Beaudry et al., 1992; Joles et al., 1994).

The linear regression analysis was conducted after the b values of the shredded cabbage, shredded lettuce, blueberries and raspberries obtained at several temperature levels were substituted into Eqs. 3·3 and 3·8. Values of $\Delta G^{\ddagger}$, E_d, and N_T were determined using the values of the intercept and slope obtained by the linear regression. Significance of the correlation coefficients between calculated linear equations and actual values was estimated by Fisher's z-transformation method with StatView® ver. 4.02 for Macintosh® (Abacus Concepts, Inc., Berkeley, USA). Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated by substituting the values of $\Delta G^{\ddagger}$ and E_d into Eqs. 3·4 and 3·5.

3.4 Results and discussion

3.4.1 Temperature dependence of O_2 consumption rate parameters of fresh produce

The O_2 consumption rate data for the shredded cabbage and shredded lettuce obtained in this study is shown in Fig. 3·1 with calculated linear lines. The O_2 consumption rate in Fig. 3·1 rose with rise of O_2 partial pressure, fall of CO_2 partial pressure, and rise of temperature surrounding the commodities. The trends agree with those described in many reports (Kader et al., 1989; Ryall and Lipton, 1979; Ryall and Pentzer, 1982). This agreement supports the supposition that the O_2 consumption rate data obtained in this study is suitable for analysis of temperature dependence of the O_2 consumption rate of the commodities. The O_2 consumption rate data for the blueberries and raspberries obtained from the literature (Beaudry et al., 1992; Joles et al., 1994) is shown in Fig. 3·2 with calculated linear lines. The temperature dependence of the O_2

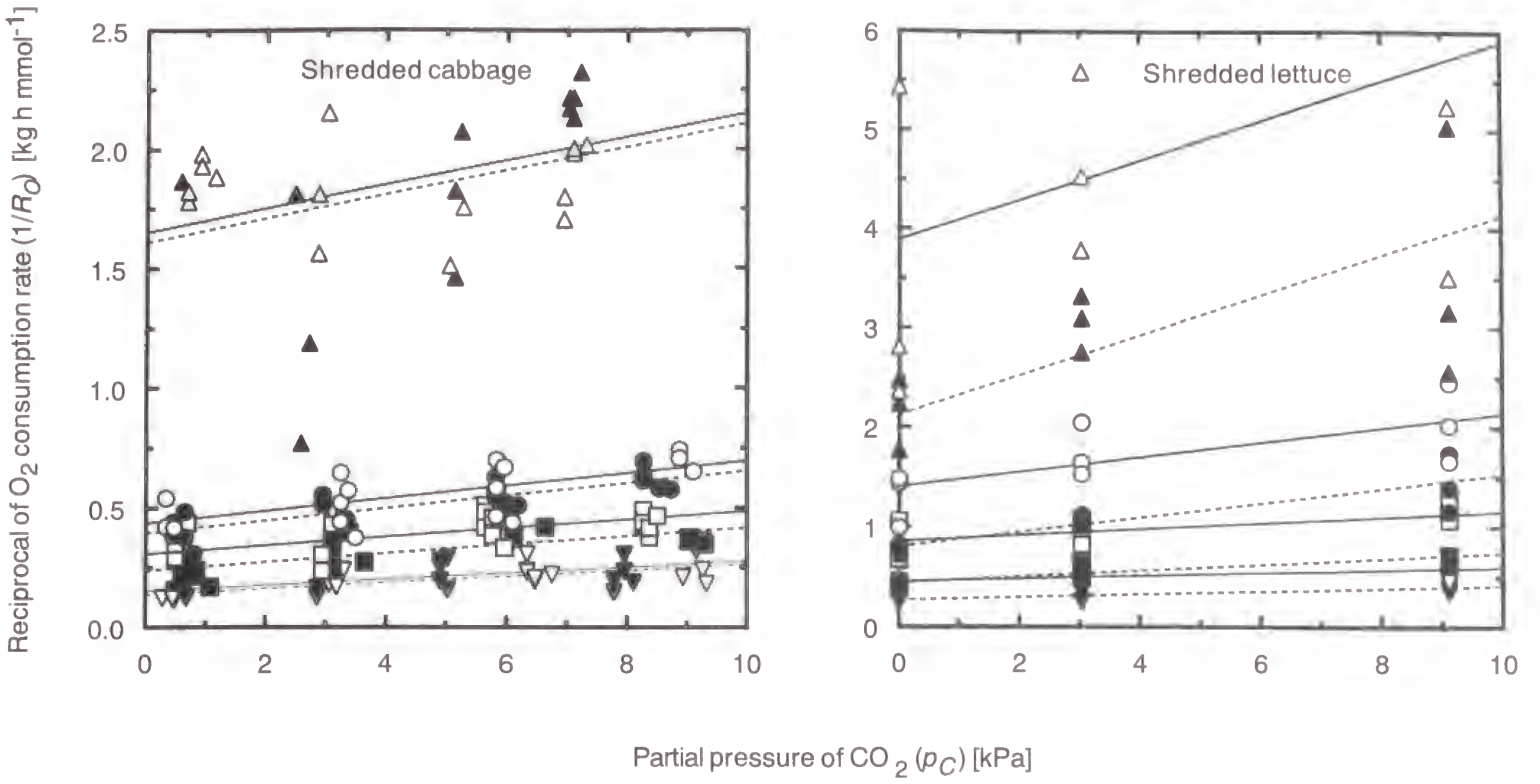

Fig. 3·1 Relationship between the reciprocal of the O_2 consumption rate ($1/R_O$) and the partial pressure of CO_2 (p_C) for shredded cabbage and shredded lettuce at 5°C (△, ▲), 15°C (○, ●), 20°C (□, ■) and 30°C (▽, ▼), where open and closed symbols denote the O_2 partial pressures of 2.03 kPa and 21.3 kPa, respectively, on the basis of the experimental data obtained in this study. Solid and dashed lines denote the linear lines generated by the method of Makino et al. (1996b) referred to the O_2 partial pressures of 2.03 kPa and 21.3 kPa, respectively.

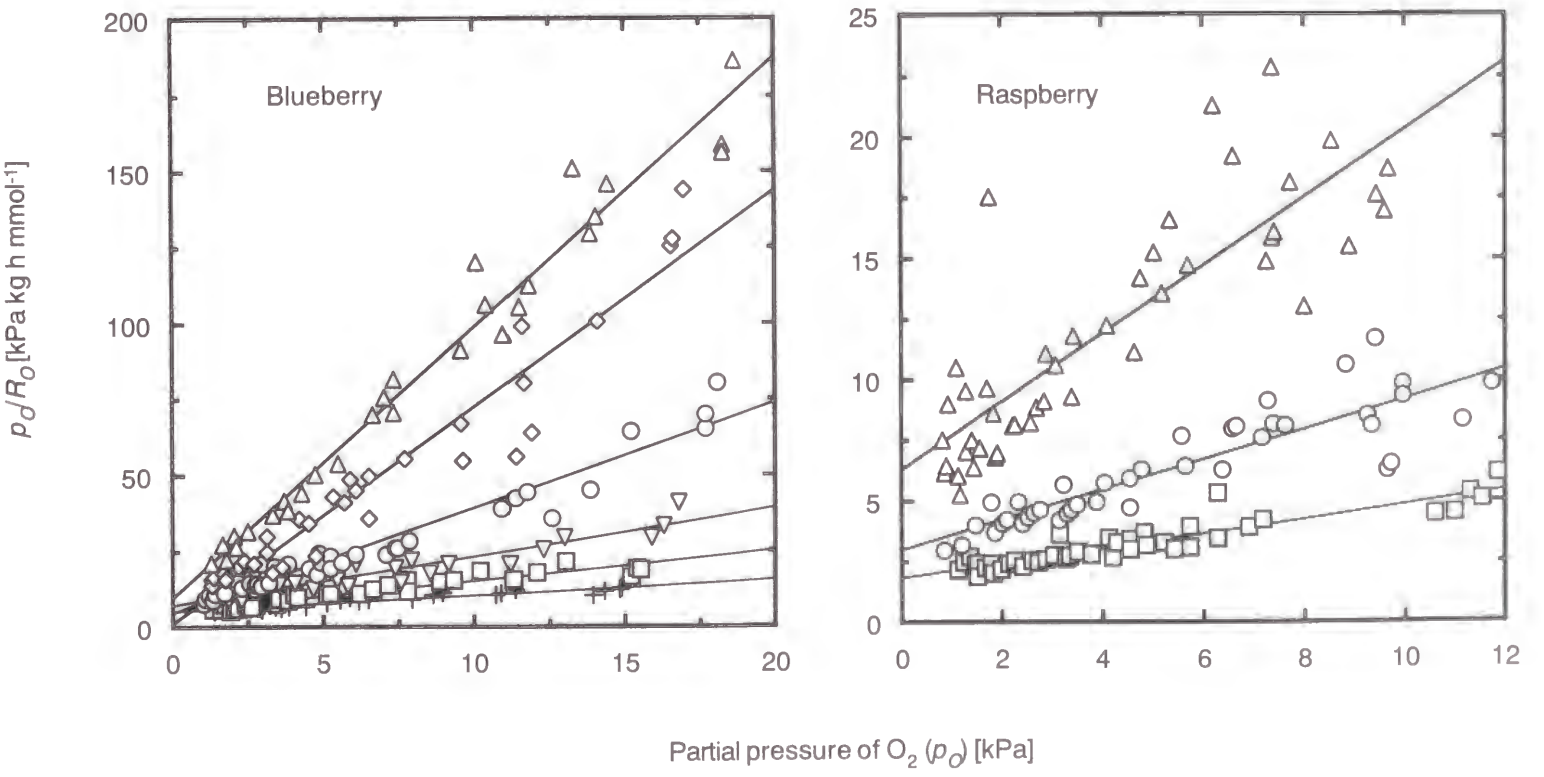

Fig. 3·2 Relationship between the product of the O_2 partial pressure (p_O) and the reciprocal of the O_2 consumption rate ($1/R_O$), and the O_2 partial pressure (p_O) for blueberry and raspberry at 0°C (△), 5°C (◇), 10°C (○), 15°C (▽), 20°C (□) and 25°C (+) on the basis of the experimental data obtained from the literature (Beaudry et al., 1992; Joles et al., 1994). Solid lines denote the linear regression lines.

consumption rate of the commodities is analyzed using the previously published data in Fig. 3·2.

The values of the parameters *a*, *b* and *i* calculated using the calculated linear lines in Figs. 3·1 and 3·2, and Eqs. 2·9–2·11 are shown in Fig. 3·3 in the same terms as Eq. 2·7. The value of *b* increased with rise of temperature. The magnitude of the rise of *b* is much larger than that of *a* or *i*. This suggests that the temperature dependence of *b* affects the temperature dependence of the O_2 consumption rate more intensively than that of *a* or *i*. According to Fig. 3·3, the effect of temperature on *a* is not clear. A change in *a* does not affect the value of the O_2 consumption rate very much because *a* is included in both the numerator and denominator of the fraction on the right side of Eq. 2·7. A change in *i* also does not affect the value of the O_2 consumption rate much because the scale of *i* is much smaller than that of *b*. The values of the parameters *a* and *i* are affected by some factors such as the velocities of O_2 and CO_2 gas diffusion through inner cells of fresh produce, solubility of the gases into cell sap, and affinities of the O_2 and CO_2 molecules for O_2 consumption sites (Makino et al., 1996b; Solomos, 1987). The factors mentioned above are dependent on the type of fresh produce. When models are constructed incorporating the temperature dependence of the parameters *a* and *i*, a very complicated equation is synthesized. The complex model is not practical for designing MAP because the calculation process is complicated. Empirical equations may be used to explain the temperature dependence of the parameters *a* and *i*. Use of the empirical models limits application area of Eq. 2·7 as a theoretical model. Average values of the parameters *a* and *i*, therefore, were used for simulation of atmosphere dynamics in MAP.

3.4.2 Thermodynamic analysis of O_2 consumption in fresh produce

Values of $\ln(b/T)$ and $\ln(b)$ calculated from the values of maximum O_2 consumption rate parameter *b* for various products are shown in Fig. 3·4. The results indicate that the

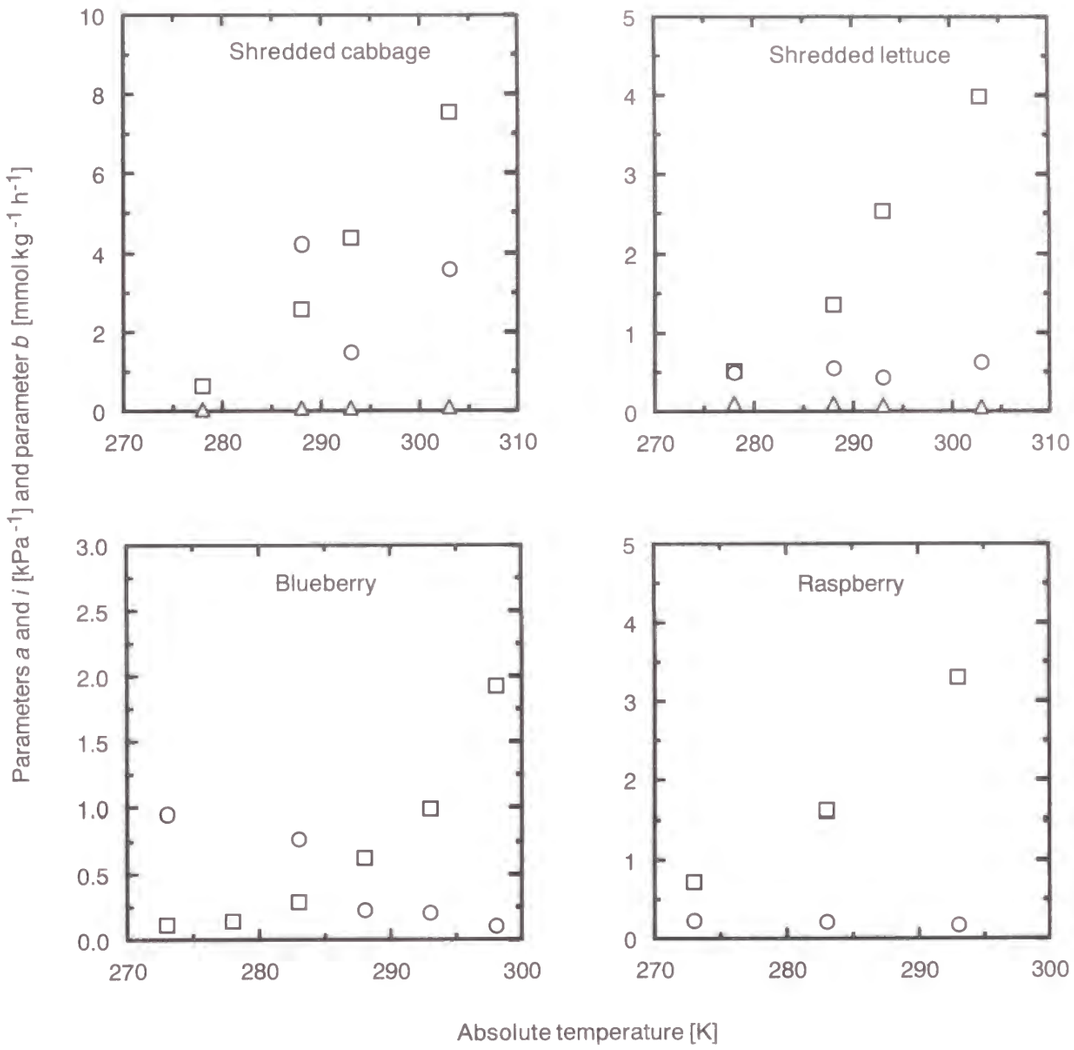

Fig. 3·3 Relationship between the respiration parameters *a* (○), *i* (△), *b* (□) and the absolute temperature.

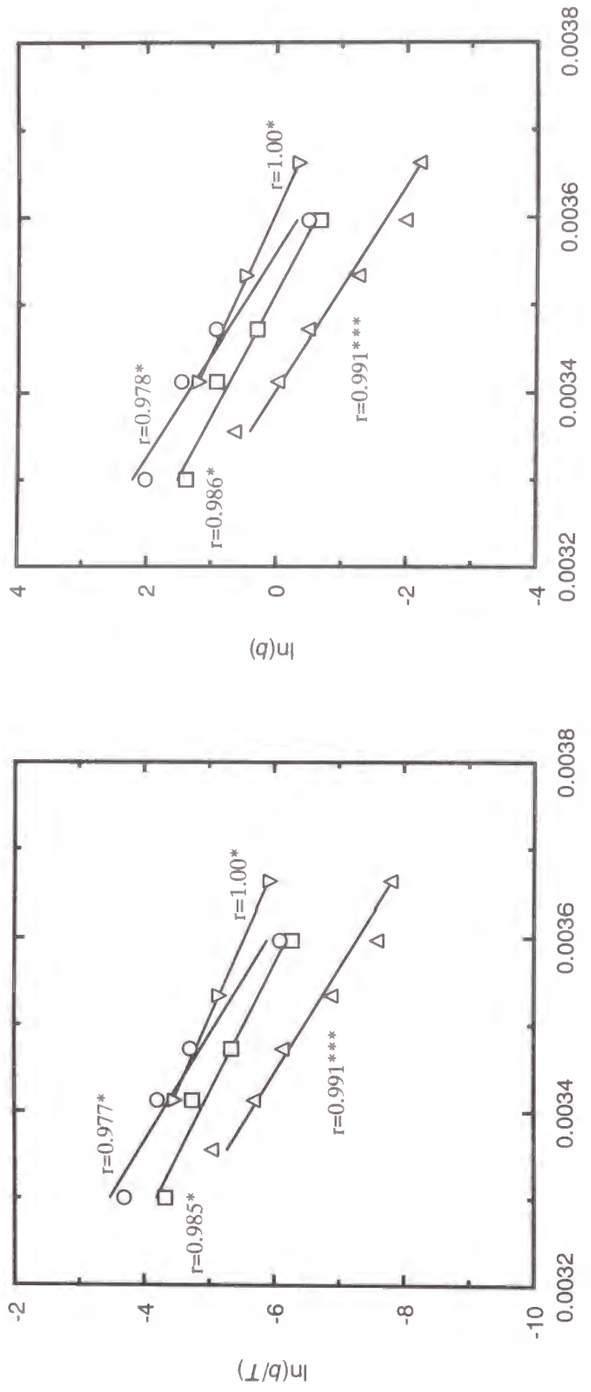

Fig. 3·4 Relationship between the natural logarithms of the respiration parameter b, the natural logarithms of b divided by the absolute temperature (T) and the reciprocal of the absolute temperature for shredded cabbage (○), shredded lettuce (□), blueberry (△) and raspberry (▽). Solid lines denote the linear regression lines. Asterisks denote the statistical significance at (*) 95% and (***) 99.9% levels by Fisher's z-transformation.

values of $\ln(b/T)$ and $\ln(b)$ linearly correlats with reciprocal of absolute temperature. These observations support the suitability of Eqs. 3·3 and 3·8 for temperature dependence of the O_2 consumption rate of the fresh produce. In the previously published reports, Karel and Go (1964), Haggar et al. (1992) and Song et al. (1992) applied the Arrhenius equation which is the same equation as Eq. 3·8 to express the respiration rates of preclimacteric hard green bananas, cut broccoli and blueberries, respectively. I applied Eq. 3·3 derived from the transition state theory. The correlation coefficients in Fig. 3·4 indicate that the proposed Eq. 3·3 is suitable for the O_2 consumption rate as well as Eq. 3·8. The Arrhenius equation, Eq. 3·8, includes the constant A_d which is difficult to explain theoretically. The symbol N_T which expresses the total number of the active sites is also included in Eq. 3·8. The proposed Eq. 3·3 is composed of Boltzmann's constant k, Planck's constant h, Avogadro's constant L and gas constant R which are generally accepted in the physicochemical area except for the symbol N_T. This suggests that Eq. 3·3 is better suited than the Arrhenius equation to describe the temperature dependence of the O_2 consumption rate from a theoretical or a universal view point.

Values of $\Delta G^{\ddagger}$, E_d, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for various products calculated using Eqs. 3·3–3·5 and 3·8 are shown in Table 3·1. The $\Delta G^{\ddagger}$ values ranged from 6.30×10^{8} (the raspberry) to 8.90×10^{8} $m^2\cdot kg\cdot h^{-2}\cdot mmol^{-1}$ (the blueberry) dependent on the kind of the commodity. The E_d values for the fresh produce are close to the $\Delta G^{\ddagger}$ values. This result agrees with the thermodynamic description that a value of Gibbs energy of activation obtained from a chemical reaction is close to the value of activation energy from the same reaction (Atkins, 1994). The values of $\Delta S^{\ddagger}$ shown in Table 3·1 are much smaller than those of $\Delta G^{\ddagger}$ or $\Delta H^{\ddagger}$. The values of the product $T\Delta S^{\ddagger}$ in Eq. 3·4 calculated from the results in Table 3·1 ranged from -1.40×10^{6} (the shredded cabbage at 30°C) to 1.53×10^{6} $m^2\cdot kg\cdot h^{-2}\cdot mmol^{-1}$ (the blueberry at 0°C) which were also much smaller than those of $\Delta G^{\ddagger}$ or $\Delta H^{\ddagger}$. This suggests that the values of $T\Delta S^{\ddagger}$ are negligible in Eq. 3·4: $\Delta G^{\ddagger}\approx\Delta H^{\ddagger}$. The

Table 3·1 Thermodynamic parameters and total numbers of active sites for O_2 consumption in fresh produce

Commodity	Temperature range	$\Delta G^{\ddagger}$	E_d	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	N_T	Reference
	(K)	($m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1}$)	($m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1}$)	($m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1}$)	($m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1} \cdot K^{-1}$)	($molecules \cdot kg^{-1}$)	
Shredded cabbage	278–303	8.81×10^8	9.12×10^8	8.79×10^8–8.82×10^8	-4.62×10^3–-4.65×10^3	7.74×10^{18}	This study
Shredded lettuce	278–303	7.28×10^8	7.59×10^8	7.27×10^8–7.29×10^8	-4.48×10^3–-4.81×10^3	3.50×10^{17}	This study
Blueberry[#1]	273–298	8.90×10^8	9.21×10^8	8.88×10^8–8.91×10^8	-3.92×10^3–-5.59×10^3	2.63×10^{18}	Beaudry et al. (1992)
Raspberry	273–293	6.30×10^8	6.61×10^8	6.29×10^8–6.31×10^8	-3.79×10^3–-3.83×10^3	2.60×10^{15}	Joles et al. (1994)
Cut broccoli	273–297	—	8.13×10^8	—	—	—	Haggar et al. (1992)
Blueberry[#2]	278–298	—	4.56×10^8	—	—	—	Song et al. (1992)
Banana[#3]	275.4–310	—	7.72×10^8	—	—	—	Karel and Go (1964)
Cassava root[#4]	277–313	—	4.88×10^8–6.51×10^8	—	—	—	Maeshima et al. (1980)

$\Delta G^{\ddagger}$ is the Gibbs energy of activation; E_d is the energy of activation for O_2 consumption in fresh produce; $\Delta H^{\ddagger}$ is the enthalpy of activation; $\Delta S^{\ddagger}$ is the entropy of activation; and N_T is the total number of active sites for O_2 consumption in fresh produce. [#1] Variety "Bluecrop". [#2] Variety "Coville". [#3] Preclimacteric hard green banana. [#4] Cytochrome c oxidase extracted from the cassava root was examined in the literature (Maeshima et al., 1980).

$\Delta H^{\ddagger}$ values were therefore very close to the $\Delta G^{\ddagger}$ values as shown in Table 3·1. The result that the value of $\Delta S^{\ddagger}$ is much smaller than the values of $\Delta G^{\ddagger}$, E_d, and $\Delta H^{\ddagger}$ included in Eqs. 3·3–3·5 and 3·8 suggests that change in entropy to activate the energy level of an O_2 molecule from a ground state to an excited state for consumption at an active site is very small (Atkins, 1994). The statement that an O_2 molecule is consumed at an active site without connection and/or disconnection among molecules (Alberts et al., 1994) also implies that the change in the value of $\Delta S^{\ddagger}$ is very small.

Values of activation energy related to respiratory reactions of fresh produce have been previously reported in the literature, however, none are available for Gibbs energy. Karel and Go (1964), Haggar et al. (1992) and Song et al. (1992) reported the values of the activation energy for preclimacteric hard green bananas, cut broccoli and blueberries, respectively as shown in Table 3·1. These are of the same order of magnitude as the E_d values in this study. The E_d values were affected by the species, the variety of the commodity, and the temperature range. Maeshima et al. (1980) reported 4.88×10^8–6.51×10^8 $m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1}$ as the value of the activation energy for a reaction of cytochrome oxidase extracted from a cassava root. Comparing this with other E_d values implies that a large part of the O_2 consumption is conducted by the cytochrome oxidase reaction in fresh produce.

The N_T values in Table 3·1 are dependent on the kind of fresh produce, which is attributed to the number of enzymes including the active sites for the O_2 consumption in fresh produce (Makino et al., 1996a). The variability is further attributed to the maturity and type of plant tissue (Ryall and Lipton, 1979; Burström, 1974). The mathematical form of Eq. 3·3 indicates that the O_2 consumption rate is determined by the values of $\Delta G^{\ddagger}$ and N_T. The O_2 consumption rate rise with fall of $\Delta G^{\ddagger}$ as $\Delta G^{\ddagger}$ expresses the potential energy needed to promote the reaction of the O_2 consumption. According to the report by Makino et al. (1996a), the O_2 consumption rate rises with rise of the N_T value. These descriptions

agree with the information obtained from the form of Eq. 3·3. This suggests that the O_2 consumption rate of fresh produce is estimated by the analytical results shown in Table 3·1. According to the values of $\Delta G^{\ddagger}$ and N_T shown in Table 3·1, I easily understand that the O_2 consumption rate of the shredded cabbage or shredded lettuce is higher than that of the blueberries. The estimation using Eq. 3·3 mentioned above is not applied to the Arrhenius equation, Eq. 3·8, including the symbol A_d. These descriptions further support that the transition state theory adopted in the present study is more effective for explaining the temperature dependence of the O_2 consumption rate of fresh produce than the Arrhenius equation adopted in the literature.

3.5 Conclusions

The feasibility of transition state theory for explaining temperature dependence of O_2 consumption rate of shredded cabbage, shredded lettuce, blueberries and raspberries was demonstrated in this study. The equation derived from the thermodynamic theory includes the total number of active sites for the O_2 consumption and generally accepted physicochemical constants such as Boltzmann's constant, Planck's constant, Avogadro's constant and the universe gas constant. The mathematical form of the derived equation indicated that the total number of the active sites and Gibbs energy of activation regulated the O_2 consumption rate of fresh produce.

PART II

Prediction of atmosphere in modified atmosphere packaging of fresh produce

Chapter 4

Measurement of gas permeability coefficients of polymeric films for modified atmosphere packaging of fresh produce

4.1 Introduction

Another important aspect in designing MAP other than respiration rate is the permeability of O_2, CO_2 and N_2 through packaging film. Measurement of the amount of a gas permeating from the higher pressure side to the lower pressure side in a closed chamber divided into two sides with the test material is a typical method to determine the gas permeability of a packaging material. The amount of the permeated gas is given by measuring the change in the pressure or volume of the gas on the lower pressure side with a manometer or coulometric sensor (Felder, 1978; Lomax, 1980). These determination methods are standardized as ASTM D1434-66M, ASTM D1434-66V, ASTM D3985-81. However, the methods need a gas transmission apparatus. Estimating the permeability on the basis of the molecular structure of a polymeric film was attempted (Lee, 1980). This method requires information on the molecular weight of the polymer.

In the present study, the development of a simple method for determining the gas permeability of polymeric films for MAP, for example, polyethylene and polypropylene, by gas chromatography was attempted.

4.2 Theoretical considerations

The gas transmission rate through a hermetically closed flexible container is expressed according to Fick's first law of diffusion and Henry's law:

$$\frac{dv_I}{dt} = \frac{P_I A}{X}(q_I - p_I) \tag{4·1}$$

where v_I is the amount of gas I in the container (mmol), t is the incubation time (h), P_I is the permeability coefficient of gas I through the container (mmol·m^{-1}·h^{-1}·kPa^{-1}), A and X are the effective area (m^2) and thickness (m) of the container, respectively, and q_I and p_I are the partial pressures of gas I outside and inside the container (kPa), respectively. When subscript I is replaced by O, C or N, it represents O_2, CO_2 or N_2 gas.

The volume of a gas in the container at an arbitrary time is as follows:

$$v_I = v_{I(0)} + \frac{P_I A}{X}\int_0^t (q_I - p_I)dt \tag{4·2}$$

where $v_{I(0)}$ is the initial amount of the gas I in the container (mmol).

p_I is assumed to be expressed by a polynomial equation:

$$p_I = \alpha_I + \beta_I t + \gamma_I t^2 + \cdots + \chi_I t^m + \cdots \tag{4·3}$$

where α_I (kPa), β_I (kPa·h^{-1}), γ_I (kPa·h^{-2}) and χ_I (kPa·h^{-m}) are the constant and coefficients of the polynomial equation, and m is the multiplier of t.

The partial pressure of gas I in the container is expressed as:

$$p_I = p\frac{v_I}{v_O + v_C + v_N} \tag{4·4}$$

where p is the overall gas pressure in the container (kPa).

When m = 2 in Eq. 4·3, the following equation is derived by substituting Eqs. 4·2 and 4·3 into Eq. 4·4.

$$\alpha_I + \beta_I t + \gamma_I t^2 = p\left\{v_{I(0)} + \frac{P_I A}{X}\int_0^t (q_I - \alpha_I - \beta_I t - \gamma_I t^2)dt\right\} \Big/ \left\{\begin{array}{l} v_{O(0)} + \frac{P_O A}{X}\int_0^t (q_O - \alpha_O - \beta_O t - \gamma_O t^2)dt \\ +v_{C(0)} + \frac{P_C A}{X}\int_0^t (q_C - \alpha_C - \beta_C t - \gamma_C t^2)dt \\ +v_{N(0)} + \frac{P_N A}{X}\int_0^t (q_N - \alpha_N - \beta_N t - \gamma_N t^2)dt \end{array}\right\} \tag{4·5}$$

The O_2, CO_2 and N_2 permeability coefficients can be calculated by solving three equations made by replacing the subscript I with O, C and N after determining α_I, β_I and γ_I.

4.3 Materials and methods

4.3.1 Test films

Gas permeability coefficients of low density polyethylene (LDPE) (thickness 1.87×10^{-5} m) and oriented polypropylene (OPP) (thickness 2.40×10^{-5} m) were examined in this study. A package (effective area 0.115 m^2) was made by heat-sealing three sides of two sheets of the test film that overlap each other. The package was closed by heat-sealing just after CO_2 gas was purged into the package. The CO_2-enriched (over 80%) package was incubated for 1 h at 15°C prior to the permeability measurement.

4.3.2 Determination of atmosphere

0.4-mL gas was periodically sampled through a silicon rubber septum glued on the surface of the incubated package, and analyzed by GC according to the method of Yamashita et al. (1989) and Hirata et al. (1993).

4.3.3 Measurement of volume of a package

The volume of the package was measured using the water displacement method.

4.3.4 Measurement of gas permeability

The O_2, CO_2 and N_2 permeability coefficients of LDPE and OPP were measured with a manometric apparatus (Gas-perm 100, Nihon Bunko Inc., Tokyo, Japan). This measurement was run in triplicate.

4.3.5 Calculation

Calculations in this study were conducted using Mathcad® ver. 3.1 (MathSoft Inc., Cambridge, USA) and a Macintosh® Centris 660AV personal computer (Apple Japan Inc., Tokyo, Japan).

4.3.6 Simulation of changes in gas concentrations

Changes in the gas concentrations in LDPE and OPP packages with broccoli were simulated using the respiration rate equation (Makino et al., 1994), permeability coefficients measured in this section and Eq. 4·1. The LDPE: an initial volume of the package and weight of broccoli are 739 mL and 0.077 kg, respectively. The OPP: an initial volume of the package and weight of broccoli are 1169 mL and 0.2 kg, respectively.

All the experimental operations in this study are repeated five times except for sub-section 4.3.4.

4.4 Results and discussion

4.4.1 Approximation of change in gas concentration with a quadratic equation

The atmospheric changes in LDPE and OPP packages with time are shown in Fig. 4·1. The CO_2 partial pressure in the packages is reduced and the O_2 and N_2 partial pressures are elevated due to the exchange of gases between the inside and outside of the packages which initially include a concentrated CO_2 gas. This suggests that the displacement of the air with CO_2 in polymeric packages is effective for simultaneously measuring the partial pressures of three gases. The permeability of a polyolefin film is quite high, especially, CO_2 permeability is estimated to be by 3–5 times higher than O_2 permeability (A Society for the Research of Plastic Films, 1974). In the present study, partial pressures of O_2, CO_2 and N_2 gases in the tested packages slowly change. This suggests that the changes fit the quadratic curves. The changes in partial pressures of gases in LDPE and OPP packages can be approximated using quadratic equations (Fig. 4·1). Values of the root mean square error (RMSE) support the accuracy of the approximation (Table 4·1). A correlation between the experimental and calculated values of the partial pressures of gases with Eq. 4·3 is shown in Fig. 4·2. The correlation coefficient ($r = 0.9999$, significant at 99%) supports the effectiveness of the approximation of changes in the partial pressures of gases with the quadratic equations.

4.4.2 Gas permeability coefficient determined by two types of methods

The gas permeability coefficient calculated using the parameters in Table 4·1 and initial volume data is presented in Table 4·2. The final time of sampling of a gas from a package is substituted into symbol t in Eq. 4·5. The gas permeability coefficient

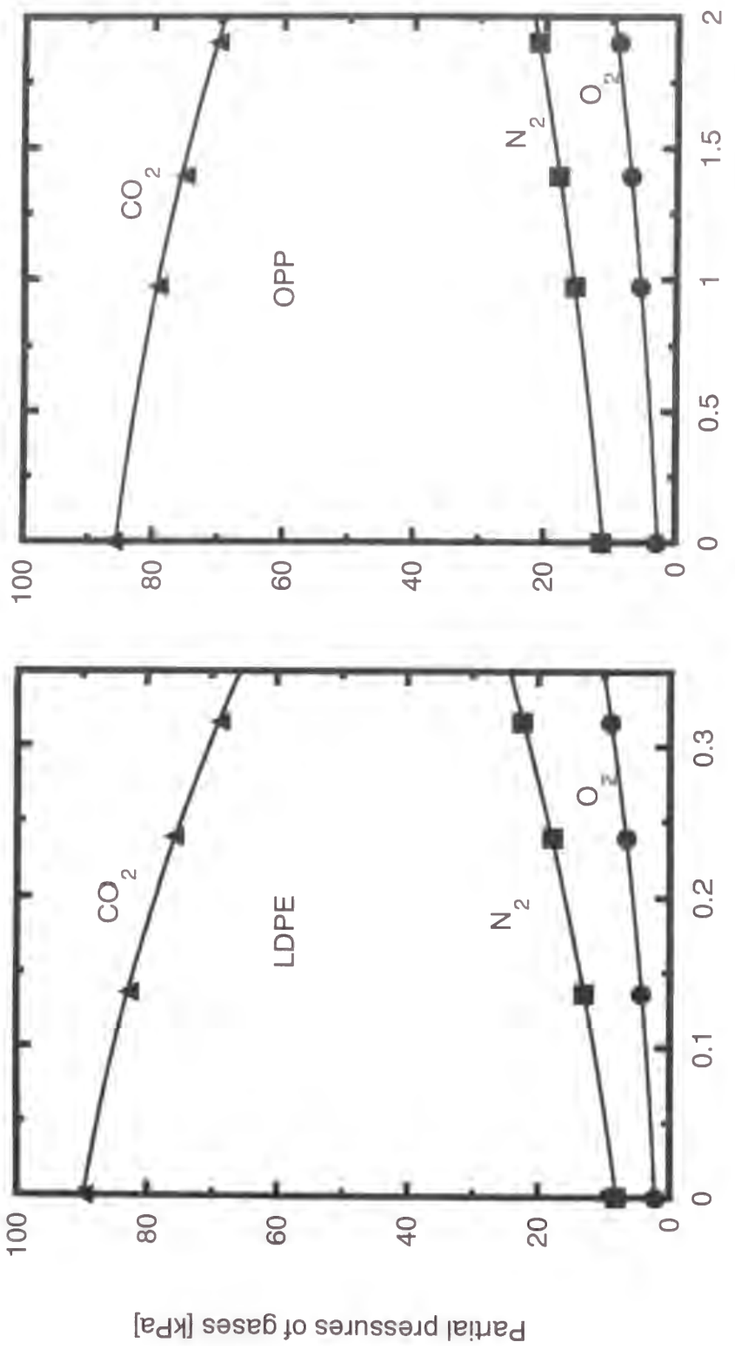

Fig. 4·1 Changes in partial pressures of gases within packages replaced with carbon dioxide.
●, ▲, ■: Experimental values
——: The best fit lines

Table 4·1

Parameters of equations expressing partial pressures of gases within packages

Film	Gas	Parameters of equation α_I (kPa)	β_I (kPa·h^{-1})	γ_I (kPa·h^{-2})	RMSE*
LDPE	O_2	2.28	10.2	35.3	1.32×10^{-2}
	N_2	8.16	30.1	48.9	7.54×10^{-3}
	CO_2	91.0	-39.4	-87.3	2.61×10^{-3}
OPP	O_2	2.72	2.17	0.683	3.74×10^{-2}
	N_2	11.0	3.94	0.780	1.25×10^{-2}
	CO_2	86.7	-4.42	-1.97	5.00×10^{-3}

* Root Mean Square Error = $\sqrt{\dfrac{\sum_{J=1}^{n}\left(D_J - D_J'\right)}{n}}$

where n: number of experimental points, D_J: experimental value of partial pressure of a gas (kPa), D_J': calculated value of partial pressure of a gas (kPa), J: type of a value.

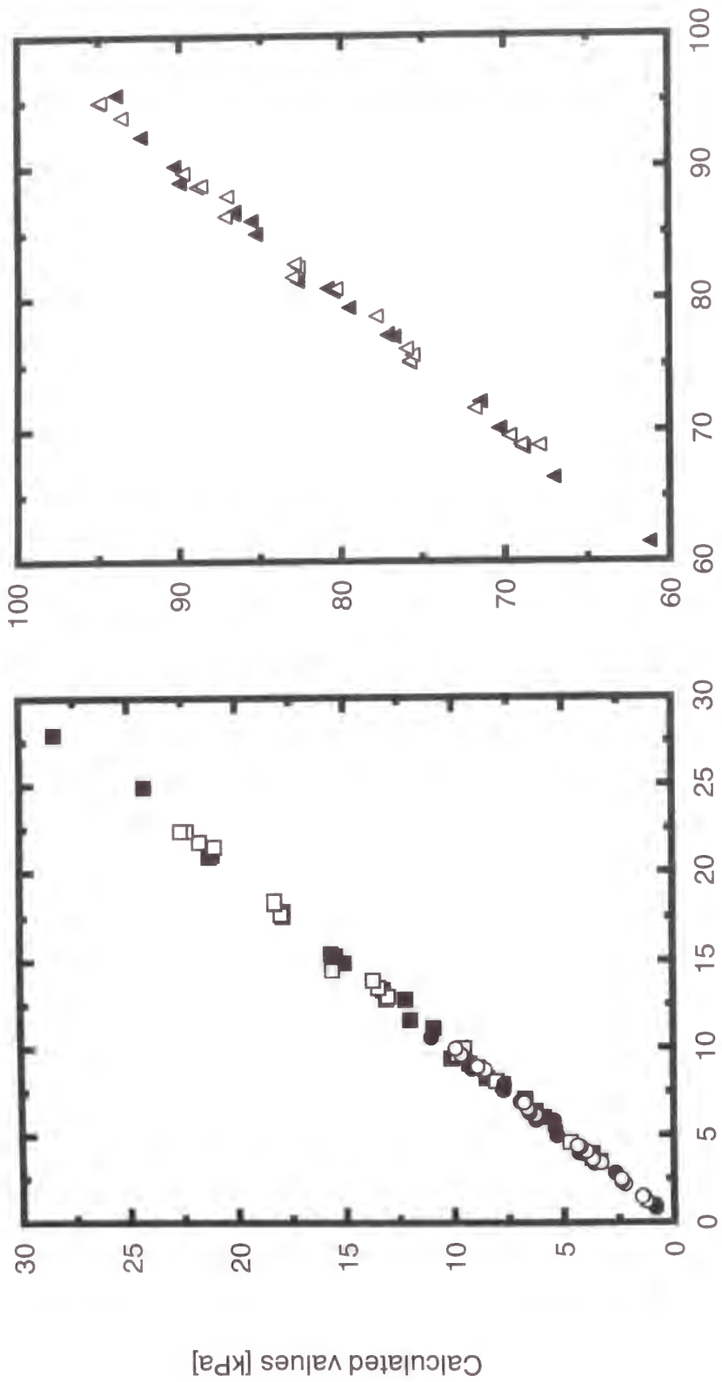

Fig. 4·2 Correlation between experimental and calculated values of partial pressures of gases within packages. ○: LDPE O_2, □: LDPE N_2, △: LDPE CO_2, ●: OPP O_2, ■: OPP N_2, ▲: OPP CO_2

measured with the manometric apparatus is also presented in Table 4·2. The differences in the coefficients between the two methods are below 22% for the O_2 and CO_2 permeability coefficients and below 46.3% for the N_2 permeability. The permeability coefficients of LDPE obtained from the simple method proposed in this study is larger than those from the apparatus. The opposite tendency appears on the permeability coefficients of OPP (Table 4·2). The differences may be caused by the variance in thickness of the tested films and the conditions of the permeability measurement. The test films are cut into circles (6 cm in diameter) for the measurement with the apparatus. However, the films are submitted to the simple method as packages. The form for the simple method is the same as the practical form for MAP with fresh produce. The heat-sealing operation or wrinkling may change the effective area of the test film thus affecting the permeability. However, the wrinkling usually occurs on the surface of a package with fresh produce. The proposed simple method is therefore suitable for determining gas permeability coefficients of polymeric films used for MAP. A gas transmission cell in the apparatus is divided into two sides with a test film. A gas is introduced into the two sides where the gas pressure on one side is higher by 0.5–1 $kg \cdot cm^{-2}$ than the other side. Changes in the pressure difference between two sides are manometrically measured with the apparatus. According to the proposed simple method, the inside and outside of a package of the test film are maintained at 1 atm. Differences in the determination method may cause the difference in the permeability between the two methods.

Simulation results of changes in gas concentrations in MAP with broccoli using the permeability coefficient values in Table 4·2 are shown in Fig. 4·3. The differences in gas concentrations (Fig. 4·3) in MAP with LDPE and OPP caused by the permeability coefficients (Table 4·2) are small. The shelf life of broccoli in MAP at 15°C is expected to be in the range 7–10 d (Makino et al., 1994). Small differences in the gas concentrations for 6 d in Fig. 4·3 suggest that the differences in the permeability

Table 4·2 Gas permeability coefficients determined by different methods at 15°C

Method	LDPE			OPP		
	O_2	CO_2	N_2	O_2	CO_2	N_2
Gas chromatography	213*	983	66.1	43.9	123	8.60
	(100)**	(100)	(100)	(100)	(100)	(100)
Gasperm-100	176	768	35.5	50.1	157	12.1
	(82.6)	(78.1)	(53.7)	(114)	(122)	(141)

* Gas permeability coefficient $\times 10^8$ mmol·m^{-1}·h^{-1}·kPa^{-1}

** Relative ratio

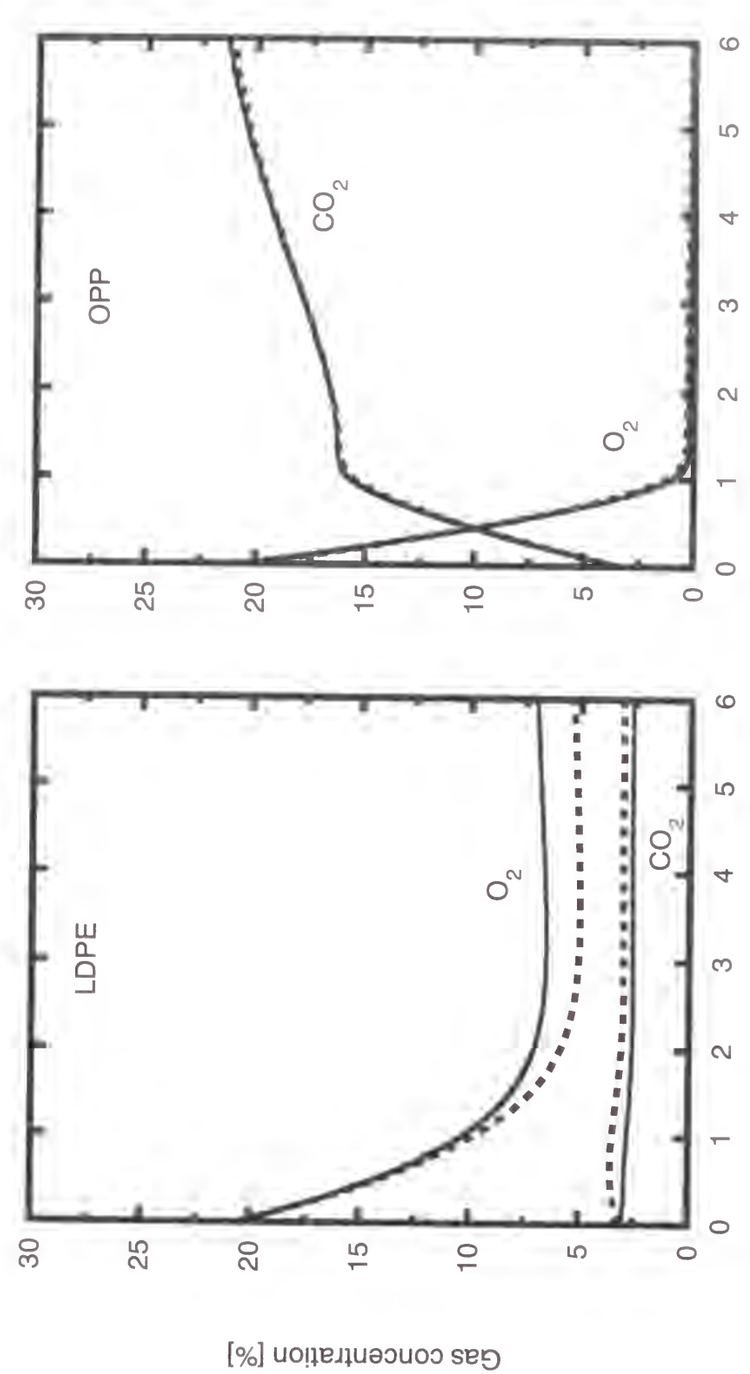

Fig. 4·3 Simulation of atmospheric changes in packages of broccoli
——: Gas permeability coefficients with a gas chromatograph
·····: Gas permeability coefficients with Gasperm-100

coefficients between the two methods (Table 4-2) can be neglected for predicting the atmosphere in MAP.

The change in gas concentration in a package is controlled by the respiration of the fresh produce and gas transmission rate of the packaging film. The effect of gas permeability on the atmosphere in MAP with a commodity of high respiration rate, for example, broccoli (ca. 70–100 mL·kg^{-1}·h^{-1}) (Forney et al., 1989; Ishikawa et al., 1992), is small. The permeability coefficients obtained from the proposed method are effective for determining the optimum packaging conditions for broccoli. The proposed method may be applied to the optimum design of packaging conditions for a commodity with a low respiration rate. The respiration models for the commodity are then needed. An allowable margin of error for the permeability coefficient obtained from the proposed method for design of the MAP conditions is also needed to explain using more permeability and simulation data.

The time for determining the permeability by measuring the change in the pressure or volume of a gas with a manometer or coulometric sensor as mentioned above (Felder, 1978; Lomax, 1980) is shorter than time of the proposed method. The permeability of polyolefin films is determined for a few hours using the manometric apparatus in this study. However, O_2, CO_2 and N_2 permeability coefficients can be simultaneously determined by the proposed method. Karel et al. (1963) simultaneously measured the O_2 and CO_2 permeability coefficients for 15 min by GC. A few samples can be examined using this method (Karel et al., 1963) as the method needs a specific transmission cell prepared for gas transmission. Many samples can be repeatedly tested by the method proposed in this study.

The permeability determination from the change in gas concentration in a package for a short time is normally performed. However, the volume of the package needs to be measured twice (once in the proposed method). The experimental operation for

determining the permeability is loaded with the excessive volume determination. The change in gas concentration in a package is generally expressed as a curve. The change is then approximated with a linear line using the normally performed method. This causes some experimental error.

The permeability of a package is determined under atmospheric pressure according to the proposed method. This suggests that the time required for measuring the permeability by the method is longer than time using a gas transmission apparatus. Therefore, the proposed method may not be effective for determining the permeability of a high-barrier material where the change in the included gas concentration is small. However, a packaging material of which the permeability is lower than OPP is rarely used for MAP as a high permeability of O_2 and CO_2 is required for MAP in order to keep a commodity under aerobic conditions (Kader et al., 1986). According to the proposed method, permeability can be determined in less than 2 d as shown in Fig. 4-1.

Chapter 5

Modified atmosphere packaging of fresh produce with a polymeric film

5.1 Introduction

The models for the O_2 consumption of fresh produce and the methods for measurements of gas permeability have been established in the former chapters. Then, in this chapter, attempts to predict dynamic changes in atmosphere in MAP systems of shredded lettuce, shredded cabbage and broccoli with polymeric pouches were made. The effectiveness of the O_2 consumption models proposed in PART I in this study was examined by the MAP test with the commodities. The simulation results of changes in O_2 and CO_2 concentrations in the systems by the models agreed with the actual values.

5.2 Theoretical considerations

In the MAP system, O_2 gas is consumed by the fresh produce, and is simultaneously replaced by the permeation through the package film from the air outside the package. The amount of O_2 gas consumed and the amount of CO_2 gas evolved per hour are calculated to be $R_O W$ and $R_C W$ [R_C is the CO_2 evolution rate of the fresh produce ($mmol \cdot kg^{-1} \cdot h^{-1}$), W is the weight of the fresh produce (kg)].

The transmission rate of O_2, CO_2 and N_2 can be calculated as $P_O A(q_O - p_O)/X$, $P_C A(q_C - p_C)/X$ and $P_N A(q_N - p_N)/X$ according to Fick's first law of diffusion and Henry's law of gas solubility, respectively. The change with time in the amount of O_2, CO_2 and N_2 molecules in this system based on material balance is presented below:

$$\frac{dv_O}{dt} = \frac{P_O A}{X}(q_O - p_O) - R_O W \tag{5·1}$$

$$\frac{dv_C}{dt} = \frac{P_C A}{X}(q_C - p_C) + R_C W \tag{5·2}$$

$$\frac{dv_N}{dt} = \frac{P_N A}{X}(q_N - p_N) \tag{5·3}$$

Temperature dependence of a gas permeability coefficient of a polymeric film is expressed by the Arrhenius equation as follows (Roberts and Kammermeyer, 1963a, b):

$$P_I = A_I e^{-\frac{E_I}{RT}} \tag{5·4}$$

where A_I is the frequency constant ($mmol \cdot m^{-1} \cdot h^{-1} \cdot kPa^{-1}$); and E_I is the energy of activation for the permeation of a gas through the film ($m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1}$). When the subscript I is replaced by O, C or N, it represents O_2, CO_2 or N_2 gas, respectively.

From R_O and R_C values, respiratory quotient (RQ) is defined as follows.

$$RQ = \frac{R_C}{R_O} \tag{5·5}$$

Atmospheric change with time in a MAP system at an arbitrary temperature included in a practical temperature range for storage of fresh produce is simulated by solving O_2 consumption rate equations and Eq. 5·1–5·5 simultaneously by the Runge-Kutta method using a microcomputer.

5.3 Materials and methods

5.3.1 Fresh produce

Shredded lettuce and shredded cabbage prepared in sub-sections 1.3.1 and 2.3.1 were submitted to MAP test with low density polyethylene (LDPE) pouches.

5.3.2 Package film for modified atmosphere packaging

A LDPE film pouch (effective area 0.072 m^2) was used for the MAP test of fresh produce. The thickness of the film was measured with a micrometer (Mitutoyo Inc., Tokyo, Japan; measurable range 0–25 mm, minimum value 0.001 mm). O_2 and N_2 gas permeability coefficients were determined at 5, 15, 20 and 30°C according to the method of Makino and Hirata (1995) using a gas chromatograph equipped with a thermal conductivity detector (Yanaco G-2800, Yanagimoto Inc., Kyoto, Japan). The data of the permeability coefficient was analyzed by linear regression using a linear equation of Eq. 5·4 [$\ln(P_I)= -(E_I)/RT+\ln(A_I)$]. A square piece of silicon rubber (1 cm^2) was attached to the surface of the package as a septum to facilitate withdrawing gas samples.

5.3.3 Determination of respiratory quotient

Respiratory quotients (RQ) of shredded cabbage and broccoli were calculated using the respiration rate data presented in Figs. 2·1 and 3·1, and Eq. 5·5.

5.3.4 Measurement of O_2 and CO_2 concentrations in MAP system

The proposed method for determining the rate of O_2 uptake was tested experimentally with MAP of shredded lettuce and shredded cabbage.

The prepared shredded lettuce (0.08 kg) and a small package of CO_2 scrubber (Ageless C®, Mitsubishi Gas Kagaku Inc., Tokyo, Japan) were enclosed in a package of LDPE film (thickness 1.62×10^{-5} m). The void volume of the package was measured according to the water displacement method, and the package was stored for 6 d at 15°C in an incubator. Oxygen concentrations within the package were periodically measured during storage by GC according to the method of Yamashita et al. (1989).

The prepared shredded cabbage (0.06 kg) was enclosed in the package of LDPE film (thickness 1.62×10^{-5} m). The void volume of the package was measured according to the water displacement method, and the package was stored for 3 d at 15°C in an incubator. The O_2 and CO_2 concentrations within the package were periodically measured during storage in the same manner as above.

A LDPE pouch (thickness 2.5×10^{-5} m) was used for a MAP test with the shredded cabbage or shredded lettuce. The prepared shredded cabbage (0.06 kg) and shredded lettuce (0.08 kg) were enclosed in the LDPE pouches. When the shredded lettuce was enclosed, a small package of CO_2 scrubber (Ageless C®) was also enclosed in the LDPE pouch as it is desirable that lettuce be stored under 0% CO_2 (Dilley, 1978). The LDPE pouch was stored for 3 d (shredded cabbage) or 6 d (shredded lettuce) at 10°C. The void volume of the LDPE pouch, and O_2 and CO_2 concentrations within the package were periodically measured during the storage by the methods described above.

Data of change in the gas concentrations in the LDPE pouch over time obtained in this study and the literature (Lee et al., 1991) was compared with the values calculated by solving O_2 consumption rate equations for fresh produce and Eqs. 5·1–5·5 using a microcomputer to estimate the practical effectiveness of the model equations proposed in the present study.

5.4 Results and discussion

5.4.1 Simulation of change in O_2 concentration in MAP

Figure 5·1 shows the change in O_2 concentration with time during the storage of shredded lettuce in the MAP system at 15°C. The O_2 concentration in the initial stage of the storage process is reduced rapidly and it reached the steady state two days after the beginning. The change in O_2 concentration was calculated as a function of time from Eqs. 1·9, 5·1 and 5·3 by the Runge-Kutta method using a microcomputer with the initial conditions of v_O 6.19 mmol, v_N 23.0 mmol, q_O 21.3 kPa, q_N 79.0 kPa, A 0.072 m^2, X 1.62×10^{-5} m, P_O 1.24×10^{-6} $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$, P_N 4.50×10^{-7} $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$, W 0.08 kg, a 0.395 kPa^{-1}, b 1.17 $mmol\cdot kg^{-1}\cdot h^{-1}$. The simulated result which is shown by a solid line in Fig. 5·1, agreed with the experimental data. This suggests that the O_2 consumption model proposed in this study may be useful for the design of the MAP system in the O_2 concentration range 2–21%. Equations 5·1 and 5·3 are valid when the gas composition in the MAP system is constant because Eq. 1·9 expresses the O_2 consumption rate during steady-state. Furthermore, the deviation of the simulated result from the experimental data during unsteady-state was very slight as shown in Fig. 5·1. This suggests that, in the case of the shredded lettuce, the gas exchange between the active sites for O_2 adsorption and the headspace is rapid due to the thin flesh of the commodity.

In the present experiment, the O_2 adsorption theory was applied to the mathematical analysis of the MAP system for shredded lettuce. This is because it is desirable to store lettuce under a 0% CO_2 concentration (Dilley, 1978). The O_2 consumption model proposed in this study is valid for limited storage conditions. However, it is preferred that some fresh produce be stored under elevated CO_2 concentration (Geeson, 1985; Ballantyne et al., 1988; Carlin et al., 1990). Further investigation of the O_2 consumption model with respect to the effects of CO_2 gas is needed in order to construct an improved practical model for designing the optimal MAP system.

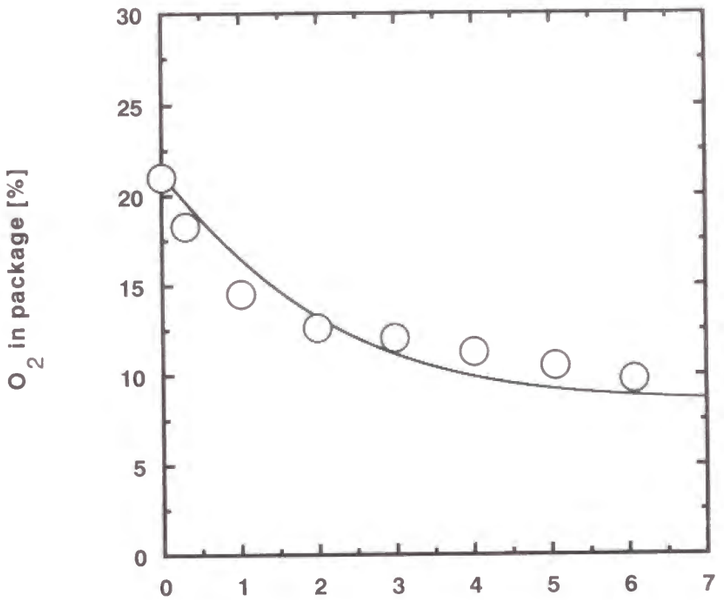

Fig. 5·1 Change in O_2 concentrations as a function of time surrounding shredded lettuce in a MAP system at 15°C. ○ denotes experimental values and the solid line refers to the simulation.

5.4.2 Simulation of change in O_2 and CO_2 concentrations in MAP

Figure 5·2 shows the change in O_2 and CO_2 concentrations with time during the storage of shredded cabbage in the MAP system at 15°C. The O_2 concentration reached 10% 1 d from the beginning and continued to reduce during storage. An O_2 concentration below 1%, which was estimated as an anaerobic condition for cabbage (Dilley, 1978), was not obtained. The CO_2 concentration was increased to almost 5% during the first day of storage and then remained almost constant during the storage. The rate change of O_2 and CO_2 concentrations were calculated from Eqs. 2·7, 5·1–5·3, and 5·5 using a microcomputer with the initial conditions of v_O 4.43 mmol, v_C 0 mmol, v_N 16.7 mmol, q_O 21.3 kPa, q_C 0 kPa, q_N 79.0 kPa, A 0.072 m^2, X 1.62×10^{-5} m, P_O 1.24×10^{-6} $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$, P_C 5.13×10^{-6} $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$, P_N 4.50×10^{-7} $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$, W 0.06 kg, RQ 0.800, a 4.2 kPa^{-1}, b 2.57 $mmol\cdot kg^{-1}\cdot h^{-1}$, and i 0.068 kPa^{-1}. The simulated result shown by the solid curves in Fig. 5·2, agreed with the experimental data. This suggests that the O_2 consumption model proposed in this study may be useful for the design of the MAP system.

Figure 5·3 shows the respiratory quotient (RQ) value of the shredded cabbage as affected by atmospheric condition, where the average was 0.800, the standard deviation (S.D.) 0.117, and the number of measurement (n) 37. According to Beaudry et al. (1992), the RQ value of fresh produce is elevated with an increase in the degree of the anaerobic condition. The anaerobic condition for the cabbage is estimated below 1% O_2 and above 10% CO_2 concentrations (Dilley, 1978). In this experiment, the atmospheric conditions used for the measurement of the O_2 consumption rate for the shredded cabbage were in the O_2 gas range of 2–21% and the CO_2 gas range of 0–9%, which were estimated as aerobic conditions. Application of an empirical equation to express the change in a RQ value limits the practical effectiveness of the theoretical models proposed in this study. The average

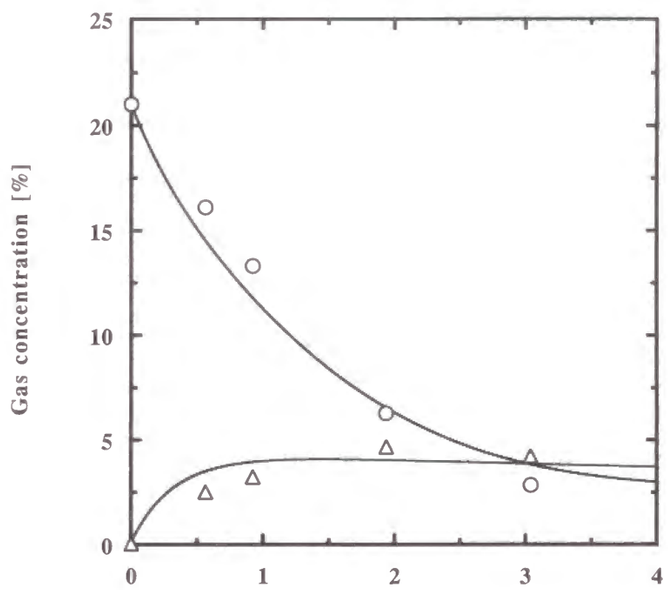

Fig. 5·2 Changes in gas concentrations surrounding the shredded cabbage with time in a modified atmosphere packaging system at 15°C. O and △ denote experimental values of O_2 and CO_2 concentrations, and the solid lines refer to the simulation.

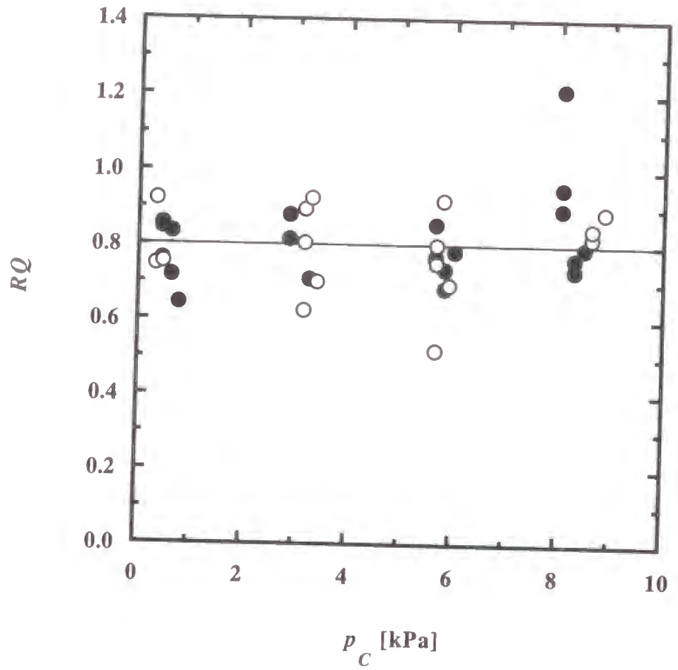

Fig. 5·3 Relationship between the respiratory quotient (RQ) and the partial pressures of O_2 (p_O) and CO_2 (p_C) surrounding the shredded cabbage. ○ at 2.03 kPa O_2, and ● at 21.3 kPa O_2.

RQ value as a typical value was therefore applied to the simulation of the atmospheric changes in the MAP system with the shredded cabbage as judged by the statistical data, the report of Beaudry et al. (1992), and the practical viewpoint. The agreement of the simulated curve for the CO_2 with the experimental data in Fig. 5·2 also supports this statement. It thus appears that this MAP system can be designed under aerobic conditions with an average RQ value.

Figure 5·4 shows the change in atmospheric condition with time during storage for the broccoli in the MAP system. The initial conditions and the experimental plots are from Lee et al. (1991). The initial conditions were v_O 5.67 mmol, v_C 0 mmol, v_N 21.4 mmol, q_O 21.3 kPa, q_C 0 kPa, q_N 79.0 kPa, A 0.072 m^2, X 5.08×10^{-5} m, P_O 2.05×10^{-6} mmol $\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$, P_C 7.21×10^{-6} $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$, P_N 6.38×10^{-7} $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$, W 0.137 kg, a 0.254 kPa^{-1}, b 12.4 $mmol\cdot kg^{-1}\cdot h^{-1}$, and i 0.0134 kPa^{-1}. The RQ value calculated from the respiration data in Fig. 2·1 was 0.707 (S.D. 0.111, n 10). The simulated result, which is shown by the solid curves in Fig. 5·4, agreed with the experimental data. This also suggests that O_2 consumption model proposed in this study may be useful for the design of the MAP system.

Yang and Chinnan (1988) employed 15 parameters to express the respiration rate of tomatoes. Sato et al. (1993) used 14 rate parameters for MAP design of broccoli. The proposed respiration model in this study employed only three parameters for MAP design of shredded cabbage and broccoli, hence the model is more practical than the two empirical models. Lee et al. (1991) used six parameters for MAP design of broccoli though the respiration model has the same mathematical form, as they expressed CO_2 evolution rate by a three parameter enzyme kinetic model. However, the CO_2 metabolism is very complicated and is also dependent on respiratory substrates in the cell sap (ap Rees, 1980). In the present study, the CO_2 evolution was expressed as RQR_O according to the definition of the RQ value. This approach may be more theoretical than the enzyme kinetic approach.

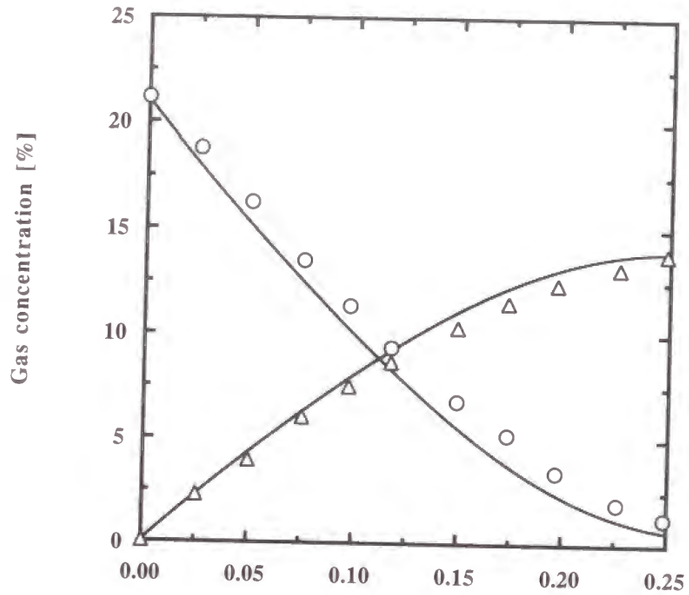

Fig. 5·4 Changes in gas concentrations surrounding broccoli with time in a modified atmosphere packaging system at 24°C. O and Δ denote experimental values of O_2 and CO_2 concentrations (Lee et al., 1991), and the solid lines refer to the simulation.

The simulated results of CO_2 concentrations in MAP systems shown in Figs. 5·2 and 5·4 are close to the experimental data. This supports the validity of the theoretical approach to the CO_2 evolution proposed in this study.

5.4.3 Temperature dependence of gas permeability of a polymeric film

Experimental data for O_2, CO_2 and N_2 permeability coefficients of a LDPE film is shown in Fig. 5·5. Values of E_I and A_I calculated by the linear regression are given in Table 5·1. These values for mine are different from those reported by Beaudry et al. (1992). This may be due to the permeability determination method, the film production method and the production lot. I regarded the values of E_I and A_I obtained in the present study are suitable for the simulation calculations of atmosphere changes in MAP systems.

5.4.4 Temperature dependence of respiratory quotient

Experimental data of *RQ* versus temperature for shredded cabbage is shown in Fig. 5·6. The statistics of *RQ* data are: mean±standard error as 0.853± 0.0163; for sample size of 138.

The temperature dependence of the *RQ* value in Fig. 5·6 is not clear. Theoretical modelling of the temperature dependence of *RQ* value is very difficult and results in complex models, because the *RQ* value changes depending on the kind of respiration substrate and metabolic pathway (Alberts et al., 1994). Application of a complex model reduces the practical usefulness of an overall simulation model. Joles et al. (1994) attempted to model the temperature dependence of the *RQ* value by an empirical approach. However, use of an empirical equation limits the application area of theoretical simulation models. Fidler and North (1967), Beaudry et al. (1992) and Joles et al. (1994) reported that the change in the *RQ* value of the fresh produce with temperature is much smaller than the change in the *RQ* value under an anaerobic condition. I, therefore, decided to adopt the

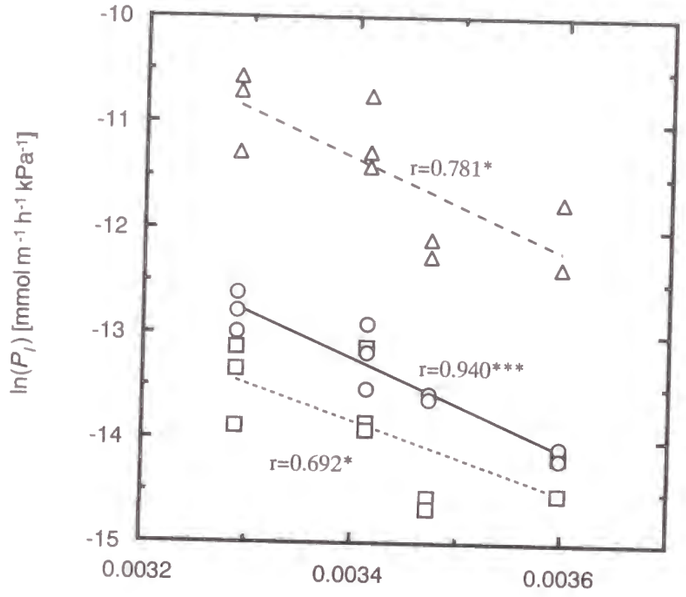

Fig. 5·5 Relationship between the permeability coefficient (P_I) of O_2 (O), CO_2 (△), N_2 (□) and the reciprocal of the absolute temperature for a low density polyethylene film. Solid, broken and dashed lines denote the linear regression lines referred to O_2, CO_2 and N_2 permeability coefficients, respectively. Asterisks denote the statistical significance at (*) 95% and (***) 99.9% levels by Fisher's z-transformation.

Table 5·1 Gas permeability parameters for low density polyethylene films

Gas	E_I ($m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1}$)	A_I ($mmol \cdot m^{-1} \cdot h^{-1} \cdot kPa^{-1}$)	Reference
O_2	4.74×10^8	5.42	This study
CO_2	3.74×10^8	44.8	This study
N_2	4.81×10^8	0.126	This study
O_2	5.16×10^8	22.7	Beaudry et.al. (1992)
CO_2	4.61×10^8	18.6	Beaudry et al. (1992)

E_I is the activation energy for gas permeation; and A_I is the frequency constant.

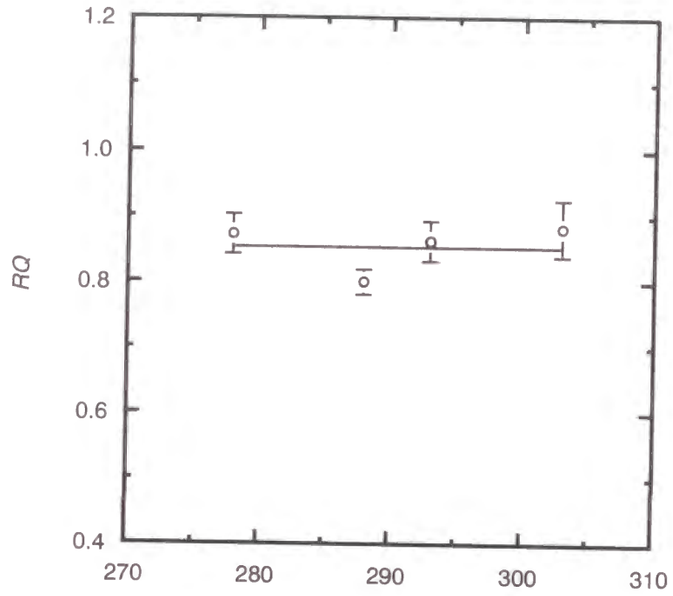

Fig. 5·6 Relationship between the respiration quotient (RQ) and the absolute temperature for shredded cabbage. Symbols (O) are means ± standard error of 28 (5°C), 37 (15°C), 35 (20°C) and 38 (30°C) experiments, respectively. Solid line denotes the average value of the overall RQ data.

average RQ value of the experimental data in simulation calculations for a MAP system with the shredded cabbage.

5.4.5 Simulation of change in atmosphere in MAP with temperature

Experimental data and simulation results (using Eqs. 2·7, 3·2 and 5·1–5·5) for changes in O_2 and CO_2 concentrations over time in the MAP systems for the shredded cabbage and the shredded lettuce at 10°C are shown in Fig. 5·7. The initial conditions were as follows: shredded cabbage—v_O, v_C, and v_N 3.16, 0 and 11.7 mmol, respectively; q_O, q_C, and q_N 21.3, 0 and 79.0 kPa, respectively; A 0.072 m^2; X 2.5×10^{-5} m; W 0.06 kg; T 283 K; parameters a and i 3.09 and 0.0691 kPa^{-1}, respectively; shredded lettuce—v_O, v_C, and v_N 7.37, 0 and 27.4 mmol, respectively; q_O, q_C, and q_N 21.3, 0 and 79.0 kPa, respectively; A 0.072 m^2; X 2.5×10^{-5} m; W 0.08 kg; T 283 K; parameters a and i 0.532 and 0.0838 kPa^{-1}, respectively. The simulation results, shown by the full lines, agreed with the experimental data quite well. This supports the proposition that the model derived from the transition state theory is suitable for expressing the temperature dependence of the O_2 consumption rate of fresh produce. This also supports the evaluations of the Gibbs activation energy, the parameters a and i, gas permeability coefficients and RQ. The assumption that the temperature dependence of the parameters a, i and of RQ is negligible is adopted to simplify the mathematical forms of the model equations, and the calculation process as described in subsections 3.2, 3.4.1 and 5.4.4 from a practical standpoint. The agreement between the experimental data and the model calculations suggests that the assumption is feasible for the design of MAP systems with fresh produce.

Morales-Castro et al. (1996a, b) calculated changes in O_2 and CO_2 concentrations over time in the MAP systems with sweet corn and head lettuce using the respiration models adaptable for change in temperature. The respiration models were constructed by the non-linear regression analysis which is an empirical approach. Deviation between the

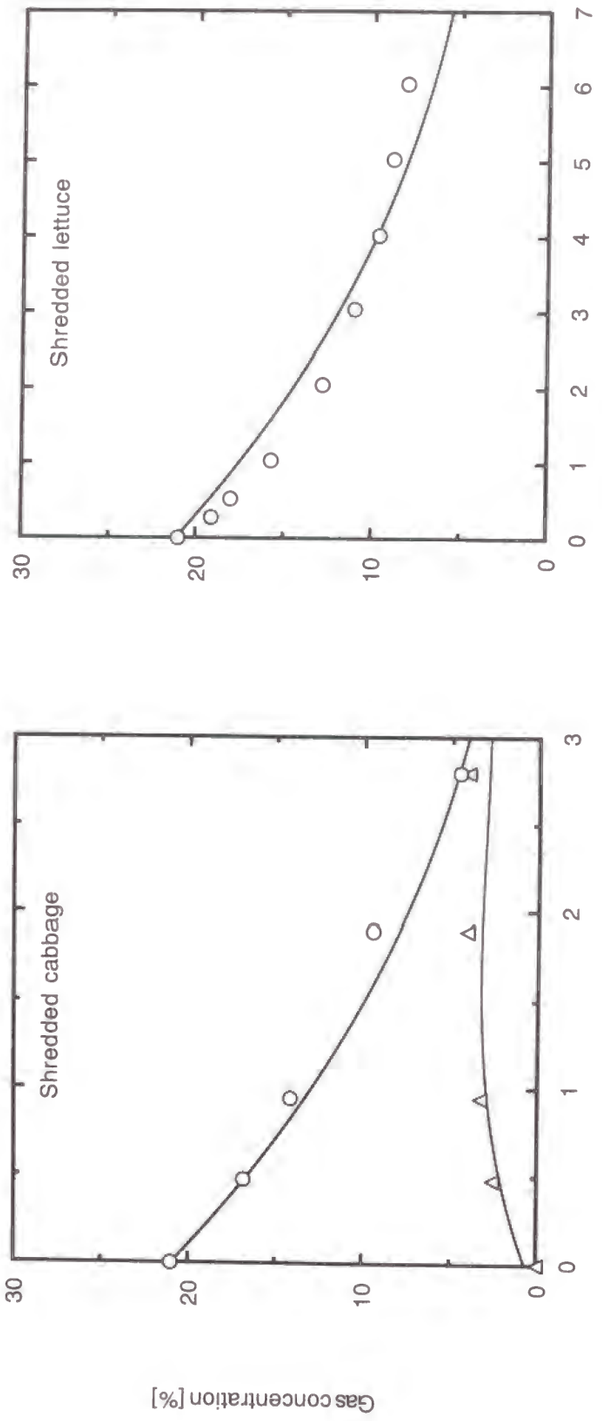

Fig. 5·7 Measured changes in concentrations of O_2 (O) and CO_2 (Δ) in modified atmosphere packaging (MAP) systems. Simulated results are shown by the full lines. The MAP system with the shredded lettuce includes a package of CO_2 scrubber (Ageless C®, Mitsubishi Gas Kagaku, Inc., Tokyo, Japan).

experimental and the simulated results was larger than that in this study. The simplified model proposed in this study, based on the transition state theory, is more effective for the design of the MAP systems than the model(s) reported in the literature.

5.5 Conclusions

The proposed O_2 consumption model and the mass balance equations were numerically solved to predict the dynamics of atmosphere in the MAP system of shredded lettuce, shredded cabbage and broccoli with low density polyethylene pouches. The simulation was conducted at 10 and 15°C. A small package of CO_2 scrubber was enclosed in the MAP system with shredded lettuce. The simulation result agreed with all the experimental data. The models was found to be valid for designing the MAP systems for fresh produce.

Chapter 6

Modified atmosphere packaging of fresh produce with a micro-perforated film

6.1 Introduction

Polymeric films have limited potential in creating different atmospheres. A CO_2-enriched atmosphere in a MAP system is difficult to be created as the transmission rate of CO_2 through a permeable film is usually higher than that of O_2. An anaerobic condition including an excessive concentration of CO_2, which caused the production of off-odor, is induced in a MAP system with a high-barrier film. Micro-perforated films have been developed to avoid inducing an anaerobic atmosphere. The micro-perforated film is indicated to be applicable to MAP for many kinds of commodities (Mannapperuma and Singh, 1993). The gas exchange through the perforations was expressed by a theoretical model based on the kinetic molecular theory of gases. No reports have been found concerning the application of this form of practical model to the MAP systems with perforations. The feasibility of the model was tested with results obtained from experiments under various conditions: temperature, perforation area, film type, initial atmosphere inside systems, and in-package commodities.

6.2 Theoretical considerations

According to Graham's law of effusion (Atkins, 1994), the amount of gas molecules which collide with unit area per unit time [μ (mmol·m^{-2}·h^{-1})] is given as:

$$\mu = \frac{p}{\sqrt{2\pi MRT}} \tag{6·1}$$

where p is the gas pressure (kPa), M the molar mass (kg·mmol^{-1}).

When a gas is present at different pressures p_1 and p_2 (kPa) on both sides of perforations where the total area is S (m^2), gas flux through the perforation q_1 (mmol ·h^{-1}) can be expressed as:

$$q_1 = S(\mu_2 - \mu_1) = \frac{S(p_2 - p_1)}{\sqrt{2\pi MRT}} \tag{6·2}$$

where μ_1 and μ_2 are the amount of gas molecules colliding with unit area per unit time at the gas pressures p_1 and p_2 (mmol·m^{-2}·h^{-1}).

Total area of the perforations is given as:

$$S = \sum_{J=1}^{n} S_J \tag{6·3}$$

where n is the number of the perforations, and S_J the area of the Jth perforation (m^2).

Gas flux into polymeric pouch through film surface [q_2 (mmol·h^{-1})] is expressed by Eq. 4·1. The net permeation into a pouch with perforations [Q (mmol·h^{-1})] is given by:

$$Q = q_1 + q_2 \tag{6·4}$$

Since gas exchange rate in a MAP system of fresh produce is determined to be a sum of the interaction between gas permeation of film and respiration of the produce, the

following equations to express the net exchange in the package with perforations are obtained:

$$\frac{dv_O}{dt} = (q_O - p_O)\left(\frac{S}{\sqrt{2\pi M_O RT}} + \frac{P_O A}{X}\right) - R_O W \tag{6·5}$$

$$\frac{dv_C}{dt} = (q_C - p_C)\left(\frac{S}{\sqrt{2\pi M_C RT}} + \frac{P_C A}{X}\right) + R_C W \tag{6·6}$$

$$\frac{dv_N}{dt} = (q_N - p_N)\left(\frac{S}{\sqrt{2\pi M_N RT}} + \frac{P_N A}{X}\right) \tag{6·7}$$

Equations 2·7 and 5·5 can be applied to the respiration of shredded cabbage, and substituted into Eqs. 6·5 and 6·6.

According to the literature reported by Renault et al. (1994b), the following models proposed by Lee et al. (1991) can be applied to the respiration of strawberries, and substituted into Eqs. 6·5 and 6·6.

$$R_O = \frac{V_m p_O}{K_m + \left(1 + \frac{p_C}{K_{i\text{-}O_2}}\right) p_O} \tag{6·8}$$

$$R_C = \frac{V_m p_O}{K_m + \left(1 + \frac{p_C}{K_{i\text{-}CO_2}}\right) p_O} \tag{6·9}$$

where V_m is the maximum respiration rate (mmol·kg^{-1}·h^{-1}), K_m the Michaelis-Menten constant (kPa), and $K_{i\text{-}O_2}$ and $K_{i\text{-}CO_2}$ the inhibition constants (kPa).

6.3 Materials and methods

6.3.1 Measurement of gas permeability through perforations

A cylindrical container (acrilic resin) used for measurement of gas permeability through perforations is shown in Fig. 6·1. An aluminum foil (diameter 0.15 m, thickness 2.5×10^{-5} m) was placed on the open side of the container, and the container was hermetically sealed by binding the foil with an acrylic resin ring immediately after CO_2 gas was flushed inside to obtain a CO_2-enriched atmosphere in the container. The aluminum foil was perforated with a thin needle (diameter 8.5×10^{-5} m), and the perforation size was microscopically determined. Ten perforations per foil were made. Each container prepared was incubated at 5.3, 14.3, and 24.9°C, and the gas compositions in the containers were periodically determined with a gas chromatograph (Hirata et al., 1993). This experiment was repeated three times at each temperature.

6.3.2 Measurement of gas permeability into pouches with a perforation

A LDPE pouch [Chori Inc., Osaka, Japan, effective area 0.114 m^2, gas permeability coefficients (mmol·m^{-1}·h^{-1}·kPa^{-1}): O_2 2.05×10^{-6}, CO_2 8.38×10^{-6}, N_2 5.42×10^{-7}, thickness 3.98×10^{-5} m] with a perforation and an OPP pouch [Toyobo Inc., Otsu, Japan, effective area 0.1026 m^2, gas permeability coefficients (mmol·m^{-1}·h^{-1}·kPa^{-1}): O_2 5.21×10^{-7}, CO_2 1.64×10^{-6}, N_2 1.26×10^{-7}, thickness 2.5×10^{-5} m] with a perforation were used as the container to determine the combined permeability through both perforation and film surface. Carbon dioxide-enriched atmosphere in the pouches was obtained by injecting the CO_2 gas through silicon rubber septum glued on the film surface. Four pouches (two LDPE and two OPP) were incubated at 15°C, and the gas compositions in the containers were periodically determined in the same manner as

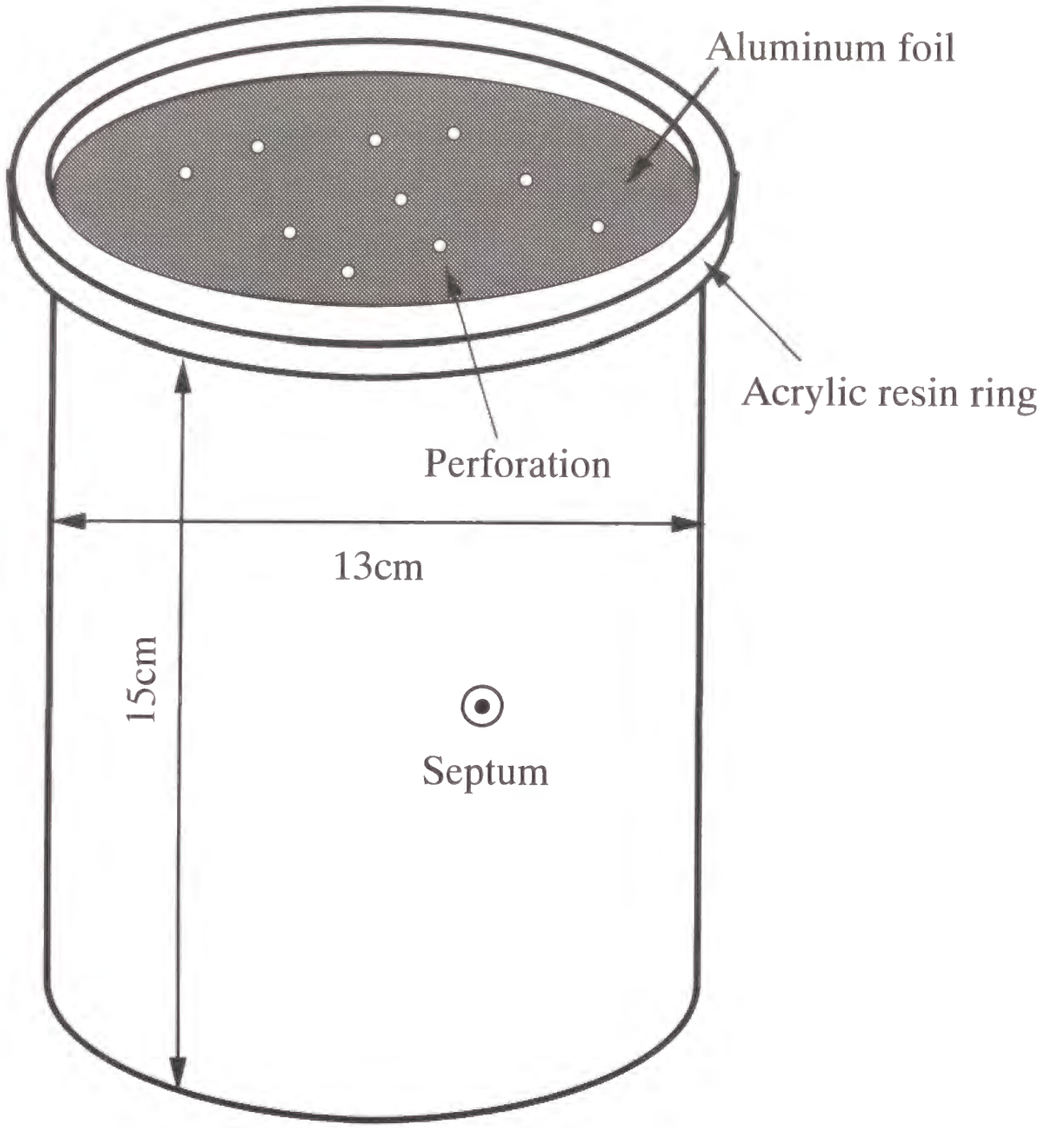

Fig. 6·1 Acrylic cylinder for the determination of gas exchange rate through perforations. Open top side of the container is covered with an aluminum foil with perforations.

mentioned above. The free volumes of the pouches were determined by the water displacement method before the pouches were perforated. The perforations were made with a thin needle, and their sizes were determined in the same manner as mentioned above. Gas permeability coefficients of the polymeric films were determined with a Gasperm-100 (Nihon bunko Inc., Tokyo, Japan).

6.3.3 Measurement of gas compositions in MAP system with a perforation

The 0.07 kg shredded cabbage (variety YR-Aoba, width 1 mm) was enclosed in an LDPE pouch [Okura kogyo Inc., Marugame, Japan, effective area 0.072 m^2, gas permeability coefficients ($mmol \cdot m^{-1} \cdot h^{-1} \cdot kPa^{-1}$): O_2 1.24×10^{-6}, CO_2 5.13×10^{-6}, N_2 4.50×10^{-7}, thickness 2.5×10^{-5} m] with a perforation, and stored at 15°C. Time changes in the gas compositions, the free volume, and the perforation size were determined in the same manner as mentioned above.

6.3.4 Computer analysis of the dynamic changes in atmospheres in the containers

Computer simulation of atmospheric changes in the containers under various conditions was carried out, and the simulated results were discussed compared with the experimental data obtained from the present study and data from the published literature by Renault et al. (1994b). All the calculations of gas compositions were executed with Mathcad® for Macintosh® ver. 3.1 (MathSoft Inc., Cambridge, USA). Correlation coefficients between experimental data and calculated results were determined using StatView® ver. 4.02 (Abacus Concepts, Inc., Berkeley, USA) and their significance was also tested by Fisher's z-transformation method with StatView®.

6.4 Results and discussion

The predicted values using Eqs. 6·5–6·7 and the experimental results of gas exchange in the acrylic cylinder with no fresh produce at 5.3, 14.3, and 24.9°C are presented in Figs. 6·2A, 6·2B and 6·2C, respectively. These temperatures cover a possible temperature range of MAP systems for fresh produce. All the predicted and measured gas concentrations correlated significantly (at 95 to 99.9% levels) with correlation coefficients ranged from 0.908 (CO_2 in Fig. 6·2C) to 0.999 (O_2, CO_2, N_2 in Fig. 6·2B). These high agreement of fit between predicted and measured gas concentrations indicate the suitability of the proposed models to predict gas exchange through perforations. The average values of area of a perforation made through the aluminum foil sheets which were incubated at 5.3, 14.3, and 24.9°C were $(7.47\pm2.97)\times10^{-9}$, $(8.27\pm5.16)\times10^{-9}$, $(9.47\pm3.96)\times10^{-9}$ m^2, respectively. The values following the sign of ± express 95% level error margin of the average value. This range of perforation size can be applied to Eq. 6·2 according to the results in Fig. 6·2.

Gas composition data analyzed with the Stephan-Maxwell equation by Renault et al. (1994b) were also calculated using Eqs. 6·5–6·7 (Fig. 6·3). Experimental data were obtained from the gas samples inside the impermeable pouches with perforations (Renault et al., 1994b). The pouches in Figs. 6·3A and 6·3B included 100% N_2 and 97% O_2 gases at zero time. All the predicted and measured gas concentrations correlated significantly (at 99.9% level) with correlation coefficients ranged from 0.923 (O_2 in Fig. 6·3A) to 0.983 (O_2 in Fig. 6·3B). These high agreement of fit between predicted and measured gas concentrations indicate the suitability of the proposed models to predict gas exchange through perforations.

When the diameter of a perforation is sufficiently small, the gas flux through the perforation is often described as either the viscous flow by the Hagen-Poiseuille law or the molecular flow by the Knudsen law (Bird et al., 1960). While in both flows, the

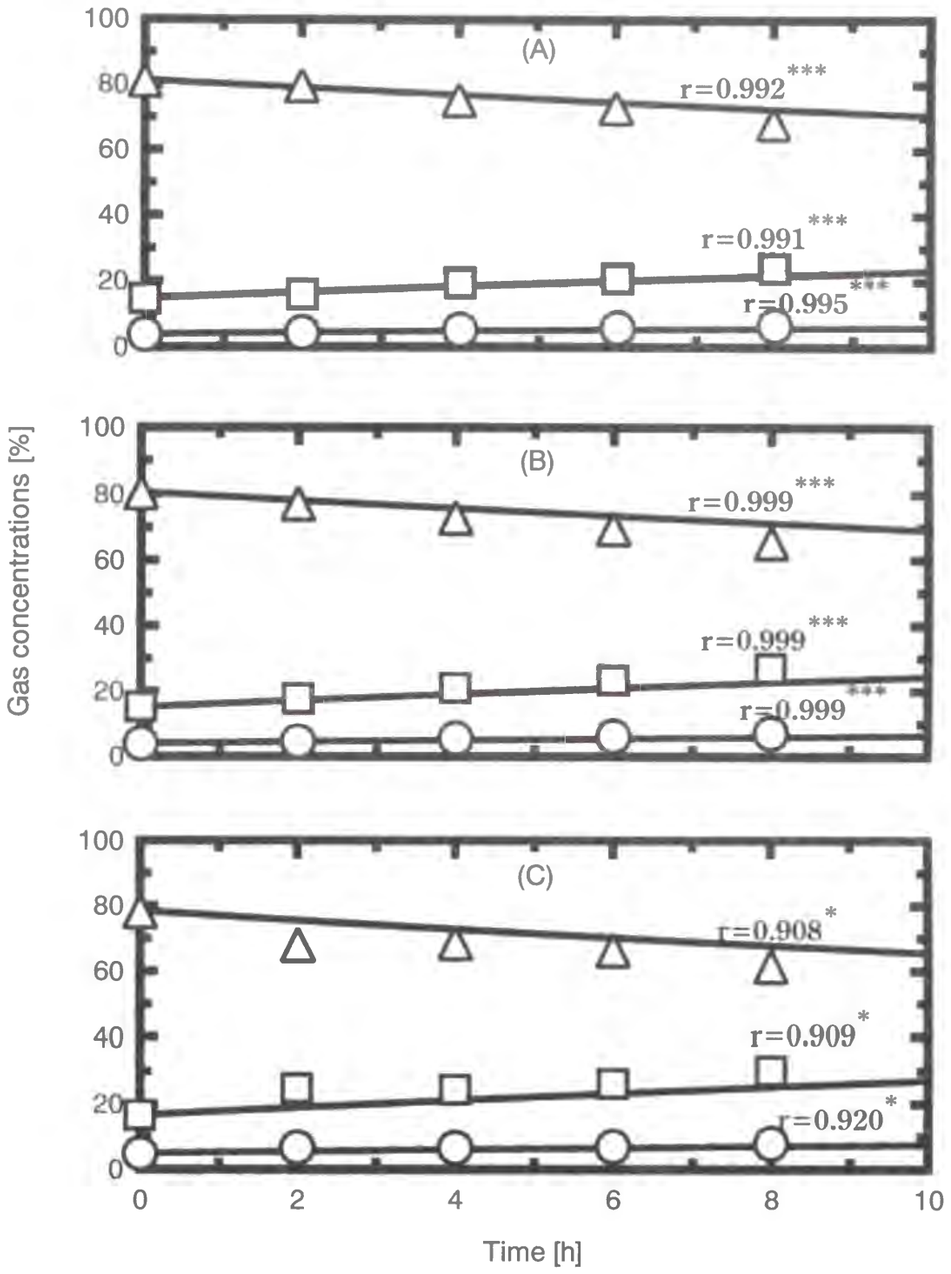

Fig. 6·2 Changes in gas concentrations of (○) O_2, (△) CO_2 and (□) N_2 in acrylic containers with perforations.

(A) 5.3°C; total area of perforations is 7.47×10^{-8} m^2; initial amount of O_2, CO_2 and N_2 molecules in the container are 3.48, 72.3 and 13.2 mmol, respectively; permeability coefficients of O_2, CO_2 and N_2 molecules through the aluminum foil are equal to 0 $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$.

(B) 14.3°C; total area of perforations is 8.27×10^{-8} m^2; initial amount of O_2, CO_2 and N_2 molecules in the container are 3.62, 71.7 and 13.5 mmol, respectively; permeability coefficients of O_2, CO_2 and N_2 molecules through the aluminum foil are equal to 0 $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$.

(C) 24.9°C; total area of perforations is 9.47×10^{-8} m^2; initial amount of O_2, CO_2 and N_2 molecules in the container are 4.14, 65.0 and 13.8 mmol, respectively; permeability coefficients of O_2, CO_2 and N_2 molecules through the aluminum foil are equal to 0 $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$.

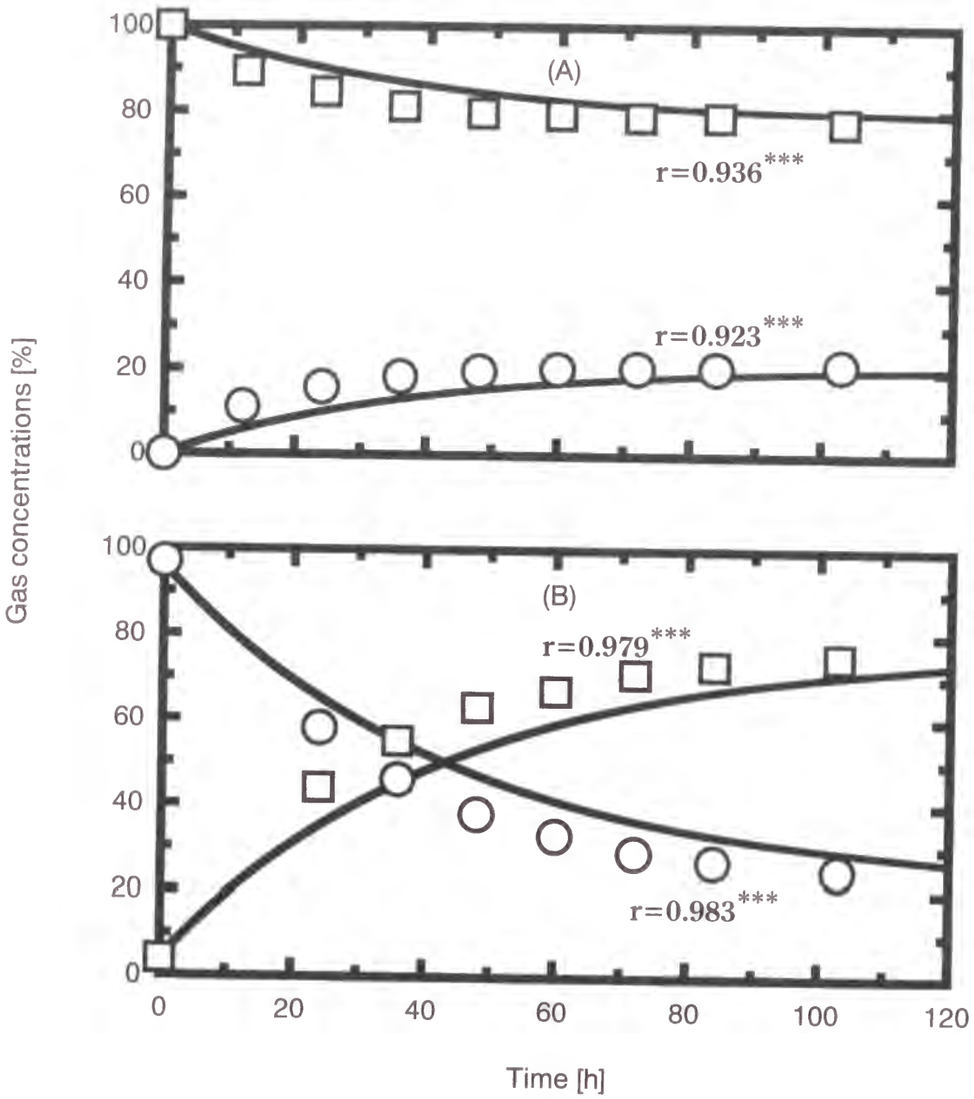

Fig. 6·3 Changes in gas concentrations of (○) O_2 and (□) N_2 in impermeable pouches with perforations at 10°C.
(A) Total area of perforations is 1.02×10^{-7} m^2; initial amount of O_2 and N_2 molecules in the pouch are 0 and 64.6 mmol, respectively.
(B) Total area of perforations is 7.75×10^{-8} m^2; initial amount of O_2 and N_2 molecules in the pouch are 62.6 and 2.0 mmol, respectively.

flux is mainly determined by the collision of flying molecules in the perforation and collision of molecules with the perforation wall, Figs. 6·2 and 6·3 suggested that Eq. 6·2 based on the kinetic molecular theory of gases is feasible for expressing the gas flux through perforations.

Using LDPE and OPP pouches with a perforation, changes in the gas composition were monitored until CO_2 concentrations decreased from ca. 90% at initial conditions to 50% (Fig. 6·4). All the predicted and measured gas concentrations correlated significantly (at 99.9% level) with correlation coefficients ranged from 0.986 (N_2 in Fig. 6·4B) to 1.00 (CO_2 and N_2 in Fig. 6·4C). These high agreement of fit between predicted and measured gas concentrations indicate the suitability of the proposed synthesized model Eq. 6·4 to predict gas exchange through polymeric pouch with perforations.

Computer simulation results of atmospheric changes in the MAP system for shredded cabbage using Eqs. 2·7, 5·5 and 6·5–6·7 are shown in Fig. 6·5A. The atmospheric change data in MAP systems for strawberries published by Renault et al. (1994b) were also analyzed using Eqs. 6·5–6·9 as shown in Figs. 6·5B and 6·5C. All the predicted and measured gas concentrations correlated significantly (at 99.9% level) with correlation coefficients ranged from 0.955 (CO_2 in Fig. 6·5A) to 0.998 (CO_2 in Fig. 6·5B). These high agreement of fit between predicted and measured gas concentrations indicate the suitability of the proposed synthesized model Eq. 6·4 to predict gas exchange through polymeric pouch with perforations for the design of MAP systems.

Equation 6·1 or 6·2 is known as Graham's law of effusion which is derived from the Maxwell-Boltzmann equation of velocity distribution based on the kinetic molecular theory of gases. In the derivation, the thickness of the perforation is assumed as naught. From the microscopic point of view, the gas molecules may fly in the

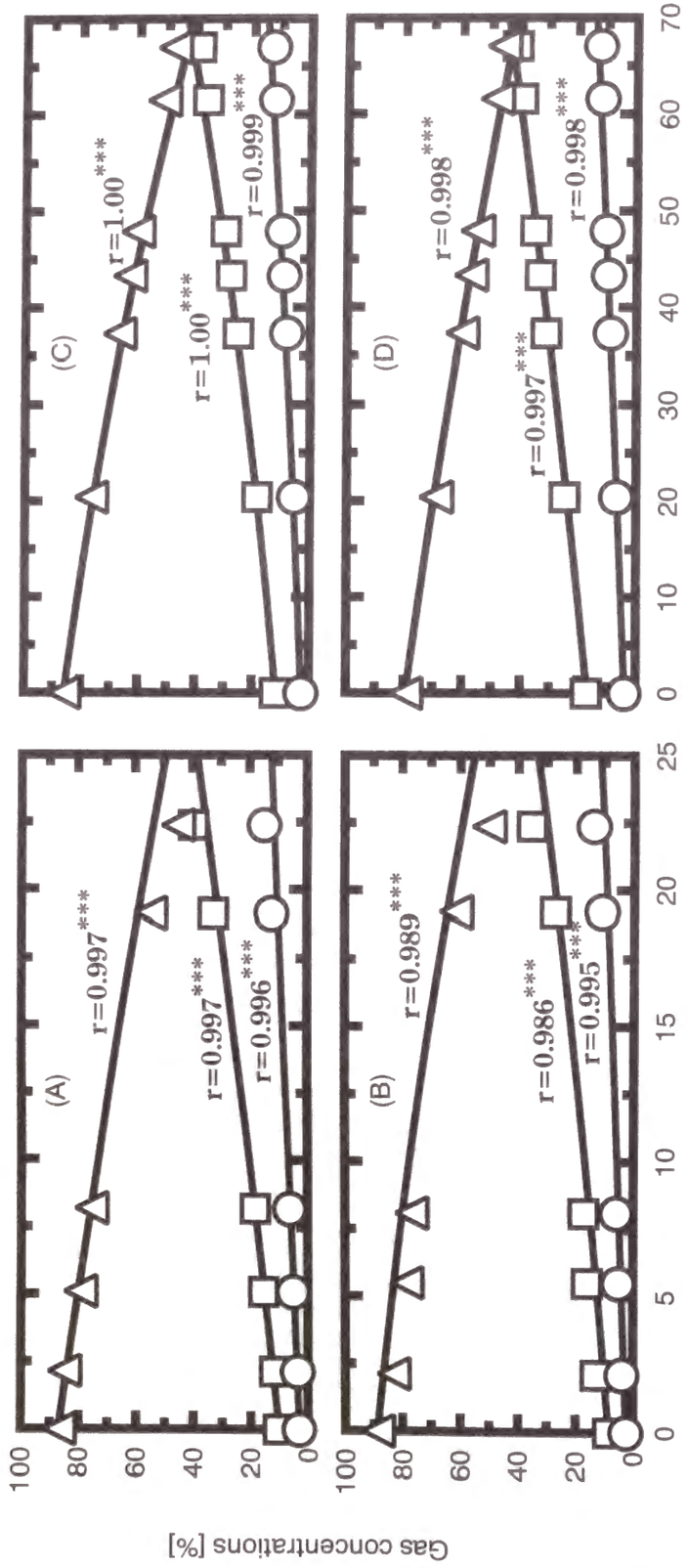

Fig. 6·4 Changes in gas concentrations of (O) O_2, (Δ) CO_2 and (□) N_2 in permeable pouches with a perforation at 15°C.
(A) LDPE film; area of a perforation is 4.91×10^{-8} m^2; initial amount of O_2, CO_2 and N_2 molecules in the pouch are 2.99, 84.1 and 9.87 mmol, respectively; permeability coefficients of O_2, CO_2 and N_2 molecules through the film are 2.05×10^{-6}, 8.38×10^{-6} and 5.42×10^{-7} $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$, respectively; thickness and effective area of the film are 3.98×10^{-5} m and 0.114 m^2, respectively.
(B) LDPE film; area of a perforation is 3.18×10^{-8} m^2; initial amount of O_2, CO_2 and N_2 molecules in the pouch are 2.47, 83.4 and 8.09 mmol, respectively; permeability coefficients of O_2, CO_2 and N_2 molecules through the film, and thickness and effective area of the film are equal to the values shown in (A).
(C) OPP film; area of a perforation is 5.67×10^{-9} m^2; initial amount of O_2, CO_2 and N_2 molecules in the pouch are 1.48, 46.5 and 6.31 mmol, respectively; permeability coefficients of O_2, CO_2 and N_2 molecules through the film are 5.21×10^{-7}, 1.64×10^{-6} and 1.26×10^{-7} $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$, respectively; thickness and effective area of the film are 2.5×10^{-5} m and 0.1026 m^2, respectively.
(D) OPP film; area of a perforation is 8.33×10^{-9} m^2; initial amount of O_2, CO_2 and N_2 molecules in the pouch are 2.54, 50.8 and 10.8 mmol, respectively; permeability coefficients of O_2, CO_2 and N_2 molecules through the film, and thickness and effective area of the film are equal to the values shown in (C).

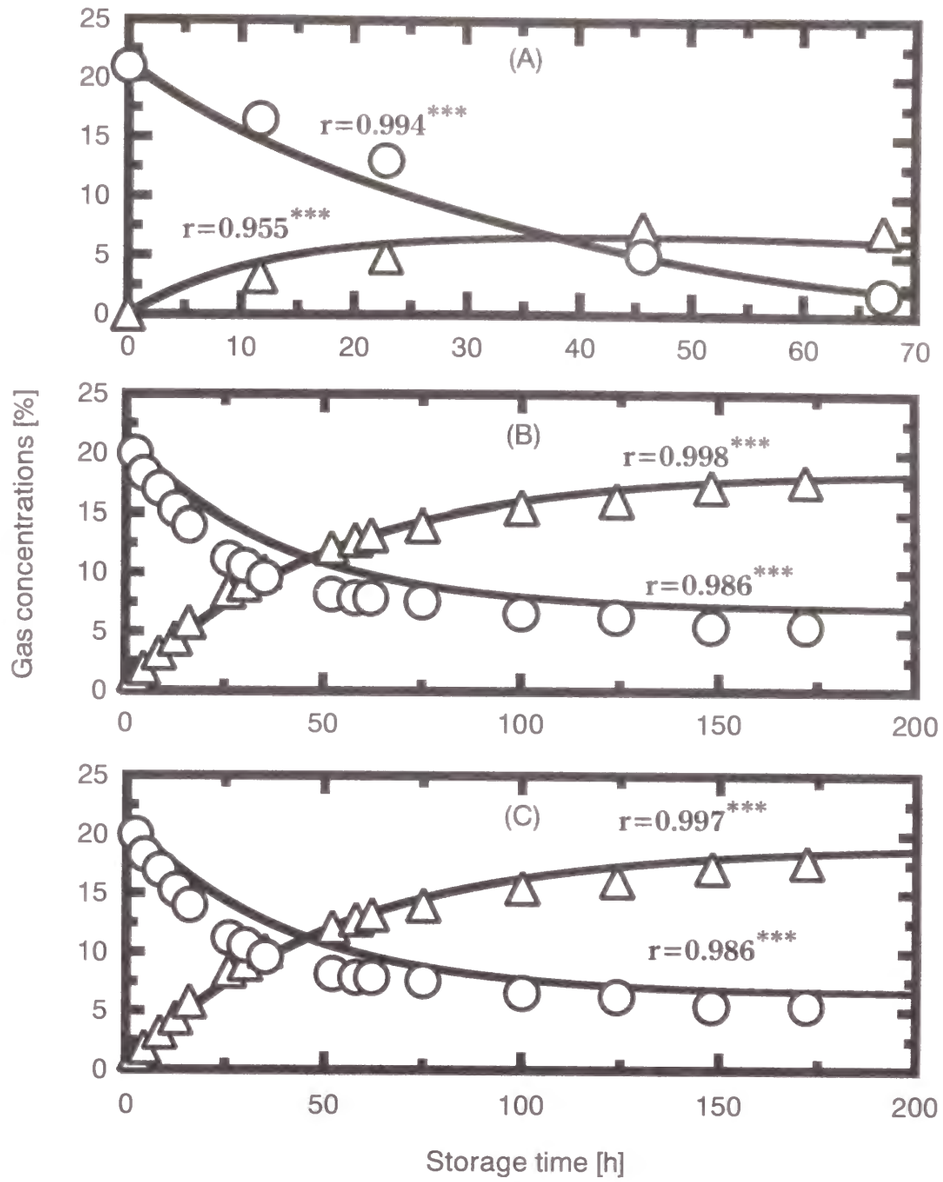

Fig. 6·5 Changes in gas concentrations of (O) O_2 and (Δ) CO_2 in MAP systems with perforations.
(A) Shredded cabbage; 15°C; area of a perforation is 9.94×10^{-9} m^2; initial amount of O_2, CO_2 and N_2 molecules in the system are 5.44, 0 and 20.2 mmol, respectively; permeability coefficients of O_2, CO_2 and N_2 molecules through the film are 1.24×10^{-6}, 5.13×10^{-6} and 4.50×10^{-7} $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$, respectively; thickness and effective area of the film are 2.5×10^{-5} m and 0.072 m^2, respectively; weight and respiration quotient of the commodity are 0.08 kg and 0.800, respectively; respiration rate parameters a, b and i are 4.20 kPa^{-1}, 2.57 $mmol\cdot kg^{-1}\cdot h^{-1}$ and 0.0681 kPa^{-1}, respectively.
(B) Strawberries; 10°C; total area of perforations is 4.42×10^{-8} m^2; initial amount of O_2, CO_2 and N_2 molecules in the system are 9.05, 0 and 33.6 mmol, respectively; permeability coefficients of O_2, CO_2 and N_2 molecules through the pouch are equal to 0 $mmol\cdot m^{-1}\cdot h^{-1}\cdot kPa^{-1}$; weight of the commodity is 0.5 kg; respiration rate parameters Km, Vm, $Ki\text{-}O_2$ and $Ki\text{-}CO_2$ are 0.2 kPa, 0.316 $mmol\cdot kg^{-1}\cdot h^{-1}$, 35.5 kPa and 81.1 kPa, respectively.
(C) Strawberries; 10°C; total area of perforations is 4.25×10^{-8} m^2; initial amount of O_2, CO_2 and N_2 molecules in the system, permeability coefficients of O_2, CO_2 and N_2 molecules through the pouch, weight of the commodity, and respiration rate parameters Km, Vm, $Ki\text{-}O_2$ and $Ki\text{-}CO_2$ are equal to the values shown in (B).

perforation with resistance by the side wall. However, I observed good agreement between predicted and actual values for gas composition changes under various conditions as shown in Figs. 6·2–6·5. This suggests that the sizes of the perforations examined in this study are described by Eq. 6·2, and that the resistance is negligible for the atmospheric changes in MAP systems. When the cross sectional area of a perforation is significantly larger than the diameter, however, another equation form may be needed for expressing the perforation flow. Equation 6·2 is a proper theoretical model because it includes only absolute values: perforation size, temperature, gas constant, and molecular weight which are obtained without empirical approaches. The simplified mathematical model, therefore, can be practical for designing MAP systems.

6.5 Conclusions

A theoretical model for designing MAP systems with perforations was developed based on Graham's law of effusion. Predicted results of gas exchange through perforations at 5.3, 14.3, and 24.9°C agreed with the actual results. Time change data found in the literature for N_2 and O_2-enriched impermeable pouches with perforations were also closely predicted using the proposed equations. Using CO_2-enriched LDPE and OPP pouches with a perforation, the in-package gas composition was periodically monitored. Calculated results of the gas composition changes with time agreed with the actual data. Simulated atmospheric changes in a MAP system for shredded cabbage agreed with actual values very well. Atmospheric conditions for strawberries in the MAP systems obtained from the literature were also accurately approximated using the proposed equations. The model proposed in this study can be useful for designing MAP systems under various environmental conditions.

Chapter 7

Modified atmosphere packaging of fresh produce with a biodegradable laminate of chitosan-cellulose and polycaprolactone

7.1 Introduction

The shelf life of fresh produce can be prolonged by modified atmosphere packaging (MAP). However, the large amount of plastic film used for food packaging creates a large waste problem. This can be reduced by optimising food packaging design, thus avoiding the excessive use of plastics. For example, the optimal conditions of a MAP system can be found by computer simulation.

Biodegradable materials for MAP may also be useful in reducing levels of waste packages in the environment. Two types of biodegradable plastics have been developed (Huang et al., 1990). One is based on chemically synthesized polycaprolactone (PCL), and the other on microbiologically synthesized polyhydroxybutyrate (PHB) (Huang et al., 1990). These biodegradable polymers have been used for absorbable surgical sutures and capsules in medicine, and as matrices for slow-release fertilizers and as containers for transplanting seedlings (Huang et al., 1990).

A biodegradable laminate produced by gluing a film made of a complex of chitosan-cellulose to a polycaprolactone film (Okura Kogyo Inc., Marugame, Japan) has been tested as a MAP film for fresh produce. Both the chitosan-cellulose complex (Hosokawa et al., 1990) and the polycaprolactone film (Tokiwa et al., 1988) were found to be microbiologically degraded. The biodegradable laminate which was developed in Japan a

few years ago has not been tested as a food packaging material. In the present study, the gas permeability of the laminate film and the film's application for MAP systems were investigated.

7.2 Materials and methods

7.2.1 Material

A laminate (thickness 5.0×10^{-5} m, Okura Kogyo, Inc., Marugame, Japan) was produced by gluing a chitosan-cellulose film (thickness 3.0×10^{-5} m, Okura Kogyo, Inc., Marugame, Japan) to a polycaprolactone film (thickness 2.0×10^{-5} m, Okura Kogyo, Inc., Marugame, Japan) as a test film. The components of the chitosan-cellulose complex film are chitosan (14.5% by weight), cellulose (48.3%), glycerol (36.2%) and protein (1.0%). Vapour permeability of the laminate measured by the method of Japanese Industrial Standard (JIS)-0208 is 7.08×10^{-3} kg·m^{-2}·h^{-1}.

7.2.2 Measurement of gas permeability coefficients of test film

Oxygen, CO_2 and N_2 gas permeability coefficients of the test film were measured by the method of Makino and Hirata (1995). The open side of a package (effective area 0.04 m^2) of the test film was closed by heat-sealing after flushing with CO_2. Each CO_2-enriched package was incubated at 10, 15 and 25°C for 24 h. A 0.4 mL gas sample was taken by syringe from an incubated package through a silicone rubber septum glued on the surface. This sampling operation was conducted four times per package during the incubation. Oxygen, CO_2 and N_2 concentrations in the gas samples were determined by GC by the method of Yamashita et al. (1989). Gas permeability coefficients of the test film at each temperature were calculated using a computer program (Mathcad® ver. 3.1 for

Macintosh®, MathSoft, Inc., Cambridge, USA). All the operations to determine the permeability coefficients were repeated three times at each temperature.

7.2.3 Calculation of gas permeability coefficients as a function of temperature

Optimal packaging for a horticultural commodity at any practical temperature can be calculated using an equation to calculate a gas permeability coefficient from the temperature.

The relationship between the gas permeability coefficient of a bi-layer laminate and that of the component mono-layer films can be derived from Fick's first law of diffusion (Bird et al., 1960):

$$\frac{X}{P}=\frac{X_1}{P_1}+\frac{X_2}{P_2} \qquad (7\cdot1)$$

where P is the gas permeability coefficient of the bi-layer laminate (mmol·m^{-1}·h^{-1}·kPa^{-1}), P_1 and P_2 the gas permeability coefficients of the mono-layer films (mmol·m^{-1}·h^{-1}·kPa^{-1}), X the thickness of the bi-layer laminate (m), and X_1 and X_2 the thickness of the mono-layer films (m).

The temperature dependence of the gas permeability coefficient of a mono-layer film can be described by the Arrhenius equation (Roberts and Kammermeyer, 1963a, b):

$$P_1 = A_1 e^{-\frac{E_1}{RT}} \qquad (7\cdot2)$$

$$P_2 = A_2 e^{-\frac{E_2}{RT}} \qquad (7\cdot3)$$

where A_1 and A_2 are the frequency constants (mmol·m^{-1}·h^{-1}·kPa^{-1}), E_1 or E_2 the activation energy (m^2·kg·h^{-2}·mmol^{-1}).

The following Eq. 7·4 can be obtained by Taylor expansion of Eq. 7·1 after substituting Eqs. 7·2 and 7·3 into Eq. 7·1:

$$P = -\frac{XA_1A_2\left(E_1X_1A_2 + E_2X_2A_1\right)}{\left(X_1A_2 + X_2A_1\right)^2 R} \cdot \frac{1}{T} + \frac{XA_1A_2}{X_1A_2 + X_2A_1} \qquad (7\cdot4)$$

The gas permeability coefficient as a dependent variable can be calculated with temperature as an independent variable. The slope and intercept of Eq. 7·4 can be calculated by linear regression analysis. In the present study, StatView® (Abacus Concepts, Inc., Berkeley, USA) was used for the linear regression analysis and for Fisher's z-transformation to evaluate significance of correlation coefficients.

7.2.4 Simulation of atmosphere dynamics in MAP systems

The change in gas composition in a MAP system for fresh produce can be modelled by Eqs. 5·1–5·3 (Jurin and Karel, 1963). The change in the gas composition inside the package with the fresh produce at any practical temperature can be calculated by solving O_2 consumption rate equations, Eqs. 7·4, 5·1–5·3 and 5·5 simultaneously.

7.2.5 MAP test for shredded lettuce and shredded cabbage

Leaves of head lettuce (variety Cisco) obtained from a wholesale produce market (Takamatsu, Japan) were shredded into square (3 cm × 3 cm) pieces. Leaves of head cabbage (variety YR-Aoba) obtained from the same market were shredded into 1 mm pieces with a cooking cutter (CQ-34, Toshiba Inc., Tokyo, Japan). The shredded lettuce and cabbage were twice washed in a stainless-pan and rinsed with a water shower for 1 min. The water adhering to the shredded leaves was removed by centrifugation (64.1 m ·s^{-2}, 30 s). The prepared shredded lettuce was enclosed in a package (effective area 0.072 m^2) of the biodegradable laminate with a small package of CO_2 scrubber Ageless C® (Mitsubishi Gas Kagaku, Inc., Tokyo, Japan), and incubated at 15°C for 6 d. The prepared shredded cabbage was enclosed in a package (effective area 0.06 m^2) of the biodegradable laminate, and incubated at 12°C for 4 d. The O_2, CO_2 and N_2 concentrations in the packages were periodically determined by GC by the method of Yamashita et al. (1989) during storage.

Change in the O_2, CO_2 and N_2 concentrations in the MAP systems was simulated by solving Eqs. 7·4, 5·1–5·3 and 5·5 simultaneously with the O_2 consumption rate equation {R_O=0.462p_O/(1+0.395p_O), 15°C} for shredded lettuce (Makino et al., 1996a), and with the O_2 consumption and CO_2 evolution rate equations {R_O=5.24p_O /(1+3.09p_O+0.213p_O·p_C), RQ=0.853, 12°C} for shredded cabbage (Makino et al., 1996b) using Mathcad® ver. 3.1 for Macintosh®. The simulated results were compared with the experimental data from the MAP experiment with shredded lettuce and cabbage.

7.2.6 Optimal design of MAP with the biodegradable laminate

Steady state O_2 and CO_2 concentrations under MAP were calculated by the graphical method (Jurin and Karel, 1963) using Eqs. 7·4, 5·1–5·3, and published respiration rate equations of head lettuce (Morales-Castro et al., 1994b), cut broccoli (Lee et al., 1991), whole broccoli (Sato et al., 1993), tomatoes (Yang and Chinnan, 1988), sweet corn (Morales-Castro et al., 1994a) and blueberries (Song et al., 1992). The optimal O_2 and CO_2 concentrations obtained by controlled atmosphere (CA) methods (Dilley, 1978; Bastrash et al., 1993) were used for the design of the MAP for each commodity. The CA method is effective for rapidly creating a desired atmosphere for a horticultural commodity because the air in the storage container is replaced by the desired gas mixture.

A 0.1m^2 effective area of the package was selected for the calculation. The weight of each commodity needed to create the optimal concentrations was calculated. The CO_2 scrubber was used with head lettuce and tomatoes because Dilley (1978) reported that zero CO_2 was suitable for these commodities.

7.3 Results and discussion

7.3.1 Temperature dependence of gas permeability of the biodegradable laminate

The temperature dependence of O_2, CO_2 and N_2 permeability coefficients of the test film is shown in Fig. 7·1 along with the results of linear regression analysis. The correlation coefficients ranged from 0.988 (CO_2 and N_2) to 0.995 (O_2) and were statistically significant at 99.9% level. The feasibility of using Eq. 7·4 to express the temperature dependence of the gas permeability coefficient of the examined laminate in the temperature range 10–25°C is supported by the results in Fig. 7·1.

The gas permeability coefficients of the bi-layer laminate can be obtained from the thickness and permeability coefficients of the component mono-layer films, although the thickness and coefficients must be determined for each mono-layer film. The permeability coefficients can also, however, be calculated using Eq. 7·4. Equation 7·4 is simpler to use than Eq. 7·1 since only one measurement of the thickness and permeability coefficient is needed for the determination of the permeability coefficient of the laminate. The accuracy of Eq. 7·4 was increased by addition of higher order terms. The parabolic relationship between CO_2 permeability coefficient and inverse of absolute temperature is shown in Fig. 7·1. However, this addition complicates the calculation procedure considerably. The results of z-transformation analysis of the permeability coefficients calculated by Eq. 7·4 in the temperature range 10–25°C confirm the accuracy of Eq. 7·4 consisting only of a first

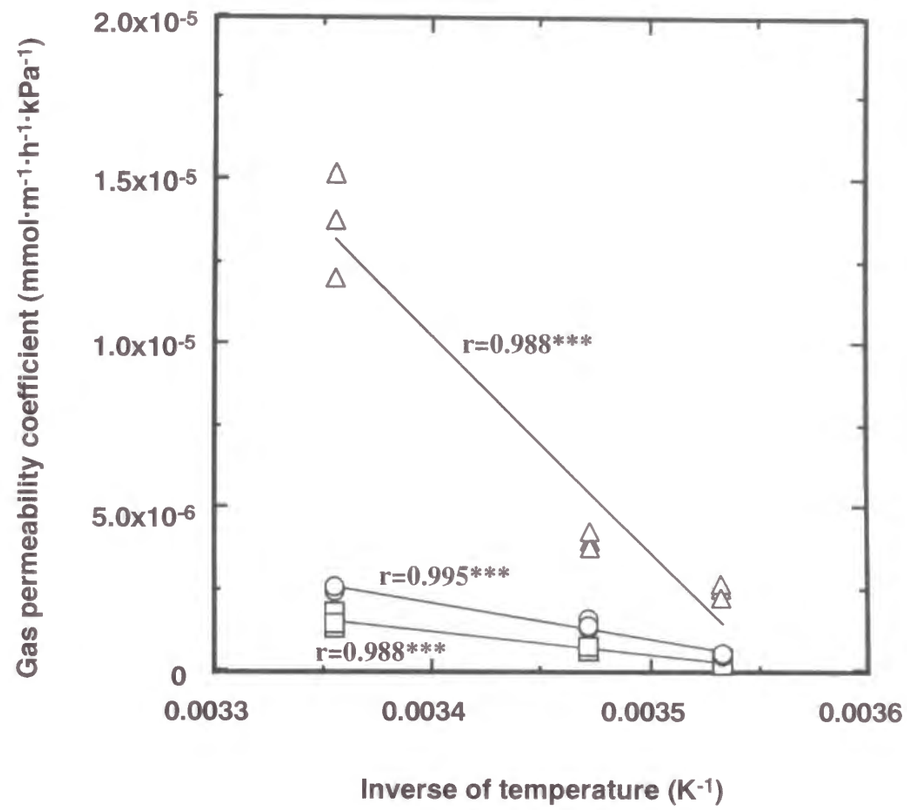

Fig. 7·1 Relationship between O_2 (○), CO_2 (△) and N_2 (□) gas permeability coefficients of a biodegradable laminate and the inverse of absolute temperature in the range 10−15℃. The slope (mmol·K·m^{-1}·h^{-1}·Pa^{-1}) and the intercept (mmol·m^{-1}·h^{-1}·Pa^{-1}) of the linear regression lines are -1.10×10^{-2} and 3.97×10^{-5} for O_2; -6.60×10^{-2} and 2.34×10^{-4} for CO_2; -6.99×10^{-3} and 2.50×10^{-5} for N_2.

order term and a constant. The higher order form may be needed for accurate calculation outside the temperature range 10–25°C. This should be investigated in the future.

The permeability coefficients of the test film at 15 and 24°C are presented in Table 7·1 with the coefficients of LDPE film. The values obtained in this study were similar to the values in the literature. Small differences in values from different researchers are probably caused by differences in production of the film, and by different measurement techniques. The values of the ratio of the CO_2 permeability coefficient to the O_2 permeability coefficient i.e. P_C/P_O for the test film are 4.17 at 15°C and 5.04 at 24°C in this study. The values for the LDPE film in the literature are 4.42 at 15°C (Sato et al., 1993) and 3.52 at 24°C (Lee et al., 1991). The value at 15°C in this study is similar to that at 15°C in the literature. Therefore, the gas composition of the biodegradable package is expected to be similar to that of the LDPE film preferred for use with fresh produce. The CO_2 permeability of the biodegradable laminate is higher than that of the LDPE film at 24°C because the value of P_C/P_O of the laminate is higher than that of the LDPE film at 24°C. The biodegradable package may not be suitable for the preservation of the CO_2 tolerant commodities at 24°C. However, this temperature level is rarely used in practice.

7.3.2 Effectiveness of proposed equations for MAP of fresh produce

The experimental data and simulated result using Eqs. 2·7, 3·2, 7·4, 5·1–5·3 and 5·5 for change in O_2, CO_2 and N_2 concentrations with time are shown in Fig. 7·2. Initial conditions were the packaging conditions when the test was started with shredded lettuce: T 288 K, v_O 4.89 mmol, v_N 18.2 mmol, A 0.072 m^2, X 5.0×10^{-5} m, q_O 21.3 kPa, q_N 79.0 kPa, W 0.05 kg; and with shredded cabbage: T 285 K, v_O 1.35 mmol, v_C 0 mmol, v_N 5.00 mmol, A 0.06 m^2, X 5.0×10^{-5} m, q_O 21.3 kPa, q_C 0 kPa, q_N 79.0 kPa, W 0.03 kg. All the calculated and measured gas concentrations correlated significantly at 99% (CO_2 for shredded cabbage) and 99.9% (except for CO_2 for shredded cabbage) with

Table 7·1 Film permeability of biodegradable laminate and low density polyethylene film (LDPE) at 15 and 24°C.

Film	Temperature (°C)	Permeability coefficient ×10^7 (mmol·m^{-1}·h^{-1}·kPa^{-1})			Reference
		O_2	CO_2	N_2	
Biodegradable laminate	15	13.0	54.2	7.06	This study
LDPE	15	12.4	–	4.50	Makino et al. (1996a)
LDPE	15	23.3	103	6.55	Sato et al. (1993)
Biodegradable laminate	24	24.8	125	1.46	This study
LDPE	24	20.5	72.1	–	Lee et al. (1991)

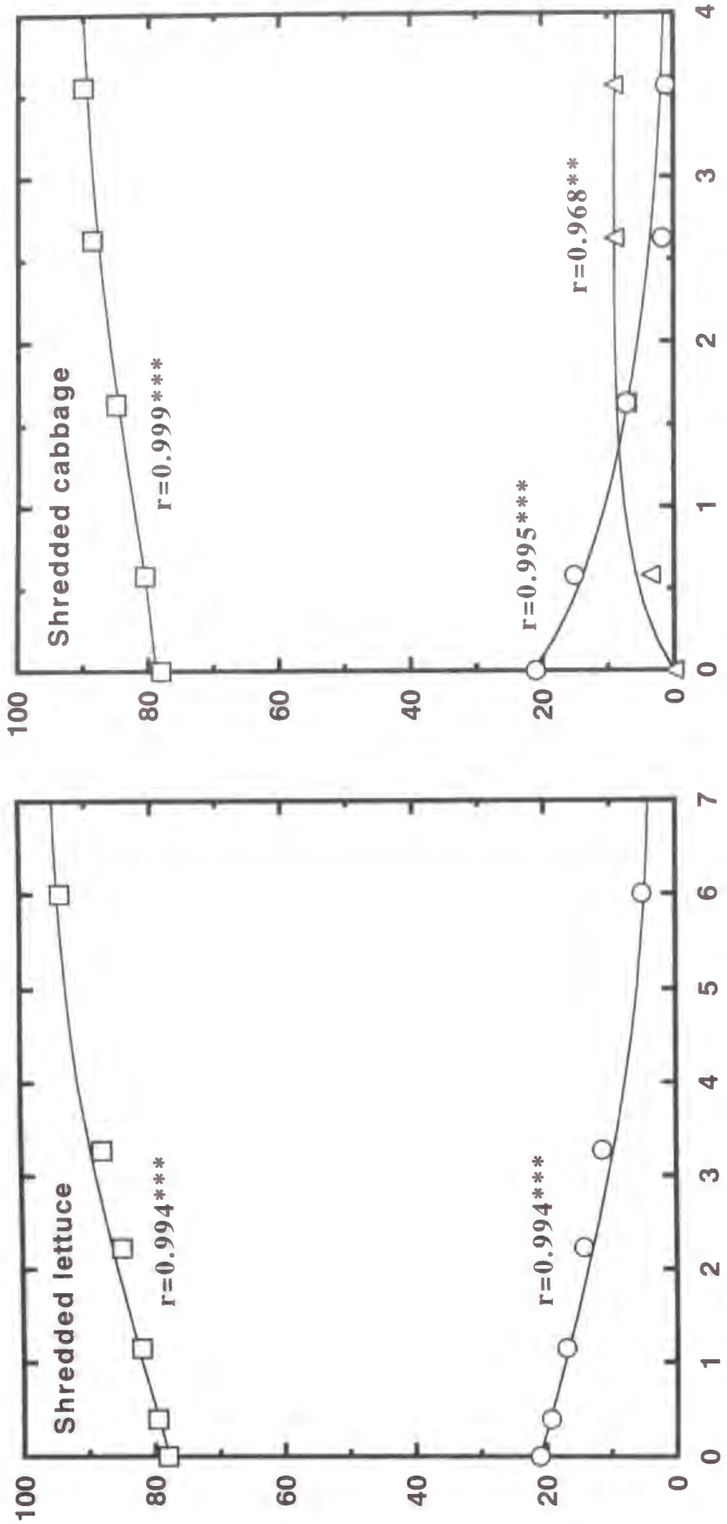

Fig. 7·2 Changes in O_2 (○), CO_2 (△) and N_2 (□) concentrations in biodegradable packages with shredded lettuce at 15°C and shredded cabbage at 12°C.

correlation coefficients ranged from 0.968 (CO_2 for shredded cabbage) to 0.999 (N_2 for shredded cabbage). This suggests that the proposed equation expressing the temperature dependence of the gas permeability coefficient, and that the values of the slope and intercept of the equation calculated were valid. This also confirms that the proposed model equations are practically effective for the design of MAP systems with fresh produce using the biodegradable package.

7.3.3 Design of MAP of fresh produce

MAP storage conditions of fresh commodities where the respiration had been evaluated in the previously published literature are shown in Table 7·2. Optimal O_2 and CO_2 concentrations in CA systems (Dilley, 1978; Bastrash et al., 1993) are also given in Table 7·2. For head lettuce and tomatoes, an O_2 concentration of 5% was calculated. This concentration is well within the allowable range (Dilley, 1978). For cut broccoli, O_2 and CO_2 concentrations of 2 and 4.14% respectively, were calculated. Bastrash et al. (1993) reported that the shelf life of cut broccoli florets could be prolonged under 2% O_2 and 6% CO_2 concentrations. The predicted gas composition is, therefore, close to the concentrations reported by Bastrash et al. (1993), and hence, is practically useful for the storage of the cut broccoli. For whole broccoli, the O_2 and CO_2 concentrations are 2.22 and 10%, respectively, which is well within the allowable range (Dilley, 1978). The value of the CO_2 permeability coefficient decreased with decreasing temperature (Fig. 7·1). The CO_2 permeability of the biodegradable package including whole broccoli (stored at 15°C), therefore, became lower than that for cut broccoli (stored at 24°C). As a result, the package used at 15°C retained a higher concentration of CO_2 than that used at 24°C. The respiration rate equation proposed by Morales-Castro et al. (1994a) could be adapted to the dynamic change in the storage temperature. The temperature and O_2 concentration for the storage of sweet corn were fixed at 25°C and 4%, respectively. A CO_2 concentration of 9.21%, well

Table 7·2 Calculated MAP conditions using a biodegradable package

Commodity	Film area (m^2)	Commodity weight (kg)	Temperature (°C)	O_2 (%) in package	CO_2 (%) in package	References of respiration rate equations
Head lettuce	0.1	0.0740	15	5 (2-5†)	0 (0†)	Morales-Castro et al. (1994b)
Cut broccoli	0.1	0.0199	24	2 (2‡)	4.14 (6‡)	Lee et al. (1991)
Broccoli	0.1	0.0645	15	2.22 (2-5†)	10.0 (10†)	Sato et al. (1993)
Tomato	0.1	0.4090	21	5 (3-5†)	0 (0†)	Yang and Chinnan (1988)
Sweet corn	0.1	0.1020	25	4 (2-4†)	9.21 (0-10†)	Morales-Castro et al. (1994a)
Blueberry	0.1	0.0260	15	10 (10†)	3.42 (11†)	Song et al. (1992)

O_2 and CO_2 (%) values parenthesized are examples of CA for storage of fresh produce

† Dilley (1978)

‡ Bastrash et al. (1993)

in the range proposed by Dilley (1978), was obtained under fixed temperature and O_2 conditions. This is practically useful for MAP storage of sweet corn. The calculated O_2 and CO_2 concentrations (10 and 3.42%, respectively) for blueberries were beyond the CA storage conditions proposed by Dilley (1978) 10 and 11%. Such an atmosphere is difficult to create by the MAP method using plastic films where CO_2 permeability is usually much higher than O_2 permeability. Emond et al. (1991) reported that 9% O_2 and 12.95% CO_2 were obtained using a perforated container. This was because the difference between O_2 and CO_2 permeability of the perforation is small. This suggests that such a high O_2-CO_2 atmosphere could be created using a perforated biodegradable package.

7.4. Conclusions

A biodegradable laminate of a chitosan-cellulose and polycaprolactone was used for MAP with horticultural commodities in the present study. The film permeability was similar to that of LDPE preferred for use with the commodities. The permeability coefficient was expressed by a linear equation as a function of temperature ranging from 10 to 25°C. The feasibility of the laminate for MAP with shredded lettuce and shredded cabbage was confirmed by computer simulation using the linear equation and experimental data. The usefulness of the laminate for MAP with head lettuce, cut broccoli, whole broccoli, tomatoes and sweet corn was tested by computer simulation using the respiration rate equations found in the published literature. The research results support the applicability of biodegradable laminate as a useful packaging material in the temperature range 10–25°C. Attempts will be made to enlarge the effective temperature range of the laminate by determination of the gas permeability and the MAP characteristics outside the range 10–25°C in the future.

Summary

The depression of respiration of fresh produce is effective for prolonging its shelf life. Modified atmosphere packaging (MAP) is used as a method to control the atmosphere in the package in order to depress the respiration activity. The rate equations for respiration of fresh produce, the transmission of gases through a packaging material and the mass balance of the gases in the package need to be modelled to determine the initial packaging conditions to create an optimum atmosphere. However, the respiration process, which is composed of many metabolic reactions, is difficult to be modelled. In the present study, attempts to effectively model the respiration process in fresh produce based on physicochemical and biochemical theories were made. The effectiveness of the proposed models for the determination of the packaging conditions was examined by predicting the atmosphere in MAP systems including horticultural commodities with some types of packaging materials using the proposed respiration models.

PART I

Chapter 1

An attempt to model the O_2 consumption process in fresh produce on the basis of chemical adsorption theory was made. A model for the O_2 consumption rate of fresh produce was derived as a function of atmospheric O_2 partial pressures based on the theory of Langmuir. The model was very effective for predicting the O_2 consumption rate of shredded lettuce, tomatoes, broccoli, apples, bananas and blueberries at 99.9% level from a statistical point of view.

Chapter 2

The inhibition mechanism of O_2 consumption in fresh produce by CO_2 reported by many researchers is that CO_2 indirectly depresses the O_2 consumption at active sites on cytochrome oxidase by inhibiting the oxidation of organic acids in the TCA cycle and of NADH in the electron transport chain. The O_2 consumption model proposed in Chapter 1 is modified by adding a term for the inhibition effect by CO_2 to the proposed model based on the reported inhibition mechanism. The modified model was very effective for predicting the O_2 consumption rates of shredded cabbage, tomatoes and broccoli under atmospheres with CO_2 at 95% level from a statistical point of view.

Chapter 3

A model to describe the temperature dependence of the O_2 consumption rate of fresh produce based on the transition state theory was proposed. The temperature dependence of the maximum O_2 consumption rate parameter included in the model proposed in Chapters 1 and 2 was expressed by the modified Eyring's equation. The derived model suggested that the O_2 consumption in fresh produce was controlled by the Gibbs free energy of activation for the O_2 consumption and the total number of active sites for the O_2 adsorption. The derived equation was very effective for expressing the temperature dependence of the O_2 consumption rate of shredded lettuce, shredded cabbage, blueberries and raspberries at 95% level from a statistical point of view.

PART II

Chapter 4

A method to determine gas permeability coefficients of materials for MAP which is needed to predict the atmosphere in MAP systems was developed. Oxygen, CO_2 and N_2 concentrations in a pouch, which initially included a CO_2-enriched atmosphere, were

periodically measured by gas chromatography. Changes in the atmosphere were expressed by quadratic equations. Gas permeability coefficients were calculated by solving mass balance equations for gases in the pouch derived from Fick's first law of diffusion and Henry's law with the quadratic equations. The difference between atmospheric changes in pouches including broccoli with polymeric films calculated using gas permeability coefficients by the proposed and manometric method with an apparatus was very small. This suggests that the proposed method is effective for the determination of the gas permeability coefficients of packaging materials for MAP of fresh produce.

Chapter 5

The O_2 consumption models for fresh produce were applied to MAP with a polymeric film. Changes in the O_2 and CO_2 concentrations in MAP of shredded lettuce, shredded cabbage and broccoli with a low density polyethylene film over time were predicted by solving the mass balance equations for gases in the MAP system with the O_2 consumption models. The simulation results agreed with the actual data obtained from the experiment.

Chapter 6

A model for transmission of a gas through a perforation was derived on the basis of Graham's law of effusion. The effectiveness of the model was confirmed by simulation of the rate of the gas transmission through micro-perforations. Changes in the O_2 and CO_2 concentrations in MAP of shredded cabbage and strawberries with perforated packaging materials over time were calculated using the rate equations for the O_2 consumption proposed in PART I and the gas transmission through micro-perforations. The simulation results agreed with the experimental data.

Chapter 7

The simulation method developed was applied to the prediction of atmosphere during MAP of fresh produce with a biodegradable laminate composed of chitosan-cellulose film and polycaprolactone film. A model for the temperature dependence of the gas permeability coefficient was proposed on the basis of Fick's first law of diffusion, the Arrhenius equation and Taylor's expansion by considering that the mono-layer films were coordinated in series for the direction of permeation of a gas. The simulation results of changes in the O_2, CO_2 and N_2 concentrations in MAP of shredded lettuce and shredded cabbage with the biodegradable laminate over time agreed with the experimental results.

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Appendix

Equations for the calculation of respiration rate parameters a, b and i can be derived from Eq. 2·8.

When the partial pressure of O_2 surrounding fresh produce is constant at p_1 (kPa), a linear equation can be obtained from Eq. 2·8 as follows:

$$\frac{1}{R_O} = A_{p1} + Bp_C \tag{A·1}$$

where A_{p1} is the intercept (kg·h·mmol^{-1}) and B the slope (kg·h·mmol^{-1}·kPa^{-1}).

The following relations are obtained from Eqs. 2·8 and A·1:

$$A_{p1} = \frac{1}{b} + \frac{1}{abp_1} \tag{A·2}$$

$$B = \frac{i}{b} \tag{A·3}$$

When the partial pressure of O_2 surrounding fresh produce is constant at p_2 (kPa), a linear equation can be obtained from Eq. 2·8 in the same manner as Eq. A·1:

$$\frac{1}{R_O} = A_{p2} + Bp_C \tag{A·4}$$

where A_{p2} is the intercept (kg·h·mmol^{-1}).

The following relation is also obtained from Eqs. 2·8 and A·4:

$$A_{p2} = \frac{1}{b} + \frac{1}{abp_2} \tag{A·5}$$

The value of the slope B in Eq. A·4 is then the same as that in Eq. A·1: $B=i/b$. This implies that the value of the slope in Eq. 2·8 is not affected by the O_2 partial pressure level.

Equations for calculation of the parameters a and b are derived from Eqs. A·2 and A·5 as follows:

$$a = \frac{A_{p1}p_1 - A_{p2}p_2}{p_1p_2\left(A_{p2} - A_{p1}\right)} \tag{A·6}$$

$$b = \frac{p_1 - p_2}{A_{p1}p_1 - A_{p2}p_2} \tag{A·7}$$

The equation for calculation of the parameter i is obtained from Eqs. A·3 and A·7 as shown:

$$i = \frac{B\left(p_1 - p_2\right)}{A_{p1}p_1 - A_{p2}p_2} \tag{A·8}$$

Notation

A	effective area of a (laminate) film	(m^2)
A_d	frequency constant	(h^{-1})
A_I	frequency constant	($mmol·m^{-1}·h^{-1}·kPa^{-1}$)
A_{p1}	constant	($kg·h·mmol^{-1}$)
A_{p2}	constant	($kg·h·mmol^{-1}$)
A_1	frequency constant	($mmol·m^{-1}·h^{-1}·kPa^{-1}$)
A_2	frequency constant	($mmol·m^{-1}·h^{-1}·kPa^{-1}$)
a	parameter	(kPa^{-1})
B	constant	($kg·h·mmol^{-1}·kPa^{-1}$)
b	maximum O_2 consumption rate	($mmol·kg^{-1}·h^{-1}$)
C_C	CO_2 concentration in a unit cell	($mmol·kg^{-1}$)
C_O	O_2 concentration in a unit cell	($mmol·kg^{-1}$)
D_J	experimental value of partial pressure of a gas	(kPa)
D_J'	calculated value of partial pressure of a gas	(kPa)
E_d	energy of activation	($m^2·kg·h^{-2}·mmol^{-1}$)
E_I	energy of activation	($m^2·kg·h^{-2}·mmol^{-1}$)
E_1	energy of activation	($m^2·kg·h^{-2}·mmol^{-1}$)
E_2	energy of activation	($m^2·kg·h^{-2}·mmol^{-1}$)
h	Planck's constant	3.98×10^{-32} $m^2·kg·h^{-1}$
I	kind of a gas	
i	parameter	(kPa^{-1})
J	type of a perforation, an active site or a value	
K_a	constant	($kg·mmol^{-1}·h^{-1}$)

K_d	constant	(h^{-1})
K_f	constant	(h^{-1})
K_i	constant	($kg \cdot mmol^{-1} \cdot h^{-1}$)
$K_{i\text{-}O_2}$	parameter	(kPa)
$K_{i\text{-}CO_2}$	parameter	(kPa)
K_m	Michaelis-Menten constant	(kPa)
k	Boltzmann's constant	4.97×10^{-20} $m^2 \cdot kg \cdot h^{-2} \cdot K^{-1}$
k_{aJ}	constant	($kg \cdot mmol^{-1} \cdot h^{-1}$)
k_{dJ}	constant	(h^{-1})
L	Avogadro's constant	6.022×10^{20} molecules·$mmol^{-1}$
M	molar mass of a molecule	($kg \cdot mmol^{-1}$)
M_C	molar mass of CO_2	($kg \cdot mmol^{-1}$)
M_N	molar mass of N_2	($kg \cdot mmol^{-1}$)
M_O	molar mass of O_2	($kg \cdot mmol^{-1}$)
m	multiplier of the symbol t	
N_A	number of O_2 molecules consumable at active sites	(molecules·kg^{-1})
N_T	total number of active sites	(molecules·kg^{-1})
n	number of perforations, types of active sites or number of values	
P	permeability coefficient of a laminate film	($mmol \cdot m^{-1} \cdot h^{-1} \cdot kPa^{-1}$)
P_C	CO_2 permeability coefficient of a film	($mmol \cdot m^{-1} \cdot h^{-1} \cdot kPa^{-1}$)
P_I	permeability coefficient of gas I through a film	($mmol \cdot m^{-1} \cdot h^{-1} \cdot kPa^{-1}$)
P_N	N_2 permeability coefficient of a film	($mmol \cdot m^{-1} \cdot h^{-1} \cdot kPa^{-1}$)
P_O	O_2 permeability coefficient of a film	($mmol \cdot m^{-1} \cdot h^{-1} \cdot kPa^{-1}$)
P_1	permeability coefficient of a mono-layer film	($mmol \cdot m^{-1} \cdot h^{-1} \cdot kPa^{-1}$)
P_2	permeability coefficient of a mono-layer film	($mmol \cdot m^{-1} \cdot h^{-1} \cdot kPa^{-1}$)
p	overall gas pressure in a MAP system	(kPa)

p_C	CO_2 partial pressure inside a MAP system	(kPa)
p_I	partial pressure of gas I inside a MAP system	(kPa)
p_N	N_2 partial pressure inside a MAP system	(kPa)
p_O	O_2 partial pressure inside a MAP system	(kPa)
p_1	constant gas pressure	(kPa)
p_2	constant gas pressure	(kPa)
Q	transmission rate of a gas through a perforated pouch	($mmol \cdot h^{-1}$)
q_C	CO_2 partial pressure outside a MAP system	(kPa)
q_I	partial pressure of gas I outside a MAP system	(kPa)
q_N	N_2 partial pressure outside a MAP system	(kPa)
q_O	O_2 partial pressure outside a MAP system	(kPa)
q_1	transmission rate of a gas through perforations	($mmol \cdot h^{-1}$)
q_2	transmission rate of a gas through a pouch	($mmol \cdot h^{-1}$)
R	gas constant	1.08×10^5 $m^2 \cdot kg \cdot h^{-2} \cdot mmol^{-1} \cdot K^{-1}$
R_C	CO_2 evolution rate of fresh produce	($mmol \cdot kg^{-1} \cdot h^{-1}$)
R_O	O_2 consumption rate of fresh produce	($mmol \cdot kg^{-1} \cdot h^{-1}$)
RQ	respiratory quotient	
S	total area of perforations	(m^2)
S_C	proportionality constant for CO_2 dissolution	($mmol \cdot kg^{-1} \cdot kPa^{-1}$)
S_J	area of Jth perforation	(m^2)
S_O	proportionality constant for O_2 dissolution	($mmol \cdot kg^{-1} \cdot kPa^{-1}$)
T	absolute temperature	(K)
t	time	(h)
V_a	O_2 adsorption rate on an active site	(molecules·$kg^{-1} \cdot h^{-1}$)
V_d	O_2 consumption rate at an active site	(molecules·$kg^{-1} \cdot h^{-1}$)
V_f	discharge rate from consumptive inhibition of O_2	(molecules·$kg^{-1} \cdot h^{-1}$)

V_i	inhibition rate of O_2 consumption at an active site	(molecules·kg^{-1}·h^{-1})
V_m	maximum O_2 consumption rate	(mmol·kg^{-1}·h^{-1})
v_C	amount of CO_2 in a MAP system	(mmol)
$v_{C(0)}$	initial amount of CO_2 in a MAP system	(mmol)
v_I	amount of gas I in a MAP system	(mmol)
$v_{I(0)}$	initial amount of gas I in a MAP system	(mmol)
v_N	amount of N_2 in a MAP system	(mmol)
$v_{N(0)}$	initial amount of N_2 in a MAP system	(mmol)
v_O	amount of O_2 in a MAP system	(mmol)
$v_{O(0)}$	initial amount of O_2 in a MAP system	(mmol)
W	weight of fresh produce	(kg)
X	thickness of a (laminate) film	(m)
X_1	thickness of a mono-layer film	(m)
X_2	thickness of a mono-layer film	(m)
x_J	number of Jth type of active sites	(molecules)
α_I	constant	(kPa)
β_I	constant	(kPa·h^{-1})
γ_I	constant	(kPa·h^{-2})
$\Delta G^{\ddagger}$	Gibbs energy of activation	(m^2·kg·h^{-2}·mmol^{-1})
$\Delta H^{\ddagger}$	enthalpy of activation	(m^2·kg·h^{-2}·mmol^{-1})
$\Delta S^{\ddagger}$	entropy of activation	(m^2·kg·h^{-2}·mmol^{-1}·K^{-1})
χ_J	constant	(kPa·h^{-m})
μ	gas molecules which collide with a unit area	(mmol·m^{-2}·h^{-1})
μ_1	gas molecules which collide with a unit area	(mmol·m^{-2}·h^{-1})
μ_2	gas molecules which collide with a unit area	(mmol·m^{-2}·h^{-1})
θ	fraction of active sites occupied by O_2 molecules	

θ_f	fraction of O_2 molecules consumable at active sites
θ_i	fraction of adsorbed O_2 molecules inhibited to be consumed at active sites

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